HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA IN THE SYSTEM ACETONE-METHANOL-WATER

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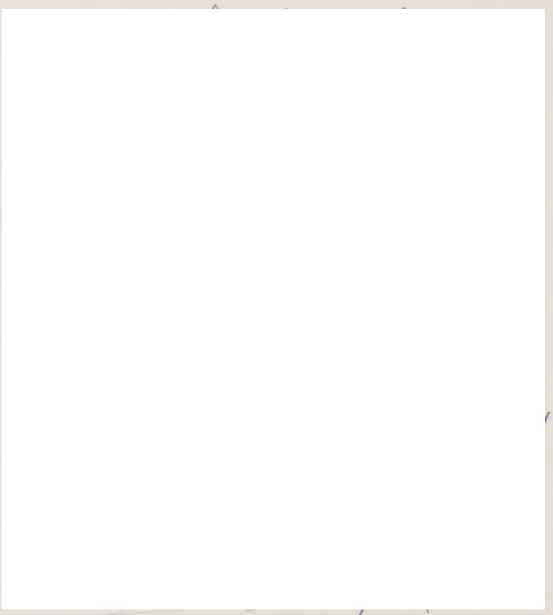

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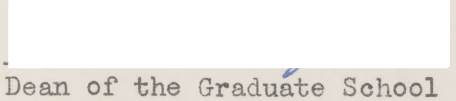

Dean of the Graduate School

HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA IN THE SYSTEM ACETONE-METHANOL-WATER

DISSERTATION

Presented to the Faculty of the Graduate School of

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PREFACE

In the field of synthetic liquid fuels and organic chemicals there is considerable industrial interest in Fischer-Tropsch-type processes for the production of liquid hydrocarbons and various organic chemicals as by-products. Processes developed primarily for the production of oxygenated organic chemicals by partial oxidation of paraffin hydrocarbons are also in commercial operation. For both processes, recovery and purification of the product constituents by fractional distillation constitute a major problem. Of primary importance to solutions of the problem are the availability of reliable vapor-liquid equilibrium data on the various systems encountered.

The need for suitable data is increased by the fact that practically all existing vapor-liquid equilibrium data are for atmospheric pressure only, whereas actual distillation operations are most frequently conducted at pressure above one atmosphere because of favorable economics, design, operations, and control requirements. It is obvious that reliable data at pressure other than one atmosphere and in particular, superatmospheric data are needed.

More fundamentally important however, is the need for complete and extended data to evaluate and test the applicability of proposed correlations of the vapor-liquid data. Such extension and correlation involve the change of vapor-liquid equilibria with temperature or pressure, the determination of these data with a minimum of experimental effort, and the extension of binary data into reliable ternary data.

Of the numerous oxygenated components produced by the aforementioned processes, acetone, methanol, and water constitute the major portion of the crude products. Binary and ternary systems containing these components have been evaluated and the results reported herein.

ACKNOWLEDGMENTS

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I

INTRODUCTION

In view of the increasing industrial importance of synthesis processes producing acetone, methanol, and water as major components in their crude products, it was decided to study the vapor-liquid equilibrium relationships of systems composed of these components. Vapor-liquid equilibrium data at atmospheric pressure for the system acetone-water have been reported by York and Holmes (42), Brunjes and Bogart (4), Othmer and Benenati (32), and Othmer and Morley (33). Isothermal data at 45°C and 60°C have been recently obtained by Soltes (38).

The system methanol-water has been investigated at one atmosphere by Cornell and Montonna (8), and also by Othmer and Benenati (32). Hausbrand (18) has also published similar data for this system. Bredig and Bayer (2) reported isothermal data at a series of temperatures.

For the system acetone-methanol at one atmosphere Othmer (31), Griswold and Buford (15) have reported the results of their investigations.

Isobaric data above one atmosphere have been published by Othmer and Morley (33) for the acetone-water and methanol-water systems. Equilibrium temperatures were not reported for the latter system.

Ternary data for the acetone-methanol-water system at 760 mm. have been determined by Griswold and Buford (15).

Vapor-liquid equilibria studies may be conducted isothermally or isobarically. For direct application of the results to rectification

processes, constant pressure data are required. Rigorous treatment in correlation, extension, and thermodynamic evaluation requires isothermal values. For small differences in boiling points, application of isothermally derived equations to isobaric data is sometimes permissible. But non-conformity between experimental and calculated results can only be attributed to mathematical inadequacy of the particular equations chosen where the values are on an isothermal basis.

The Margules 3-suffix ternary equation has been found to correlate certain immiscible C_4- hydrocarbon-furfural systems by Gerster, Mertes, and Colburn (13). It was decided to give this particular equation a rather severe and complete test to see how well it might apply to miscible aqueous organic systems. For this purpose, the complete binary and ternary vapor-liquid equilibrium isotherms for acetone, methanol, and water have been calculated at several temperatures and compared with experimental data.

II

THEORETICAL CONSIDERATIONS

Thermodynamic Activity Coefficients

In the simplest case of vapor-liquid equilibrium, the components form an ideal solution and the vapors do not deviate from ideality. The three general criteria which are most useful for experimental evaluation of such solutions are:

(1) Negligible volume changes on mixing

(2) Negligible heats of solution on mixing

(3) The total vapor pressure or partial pressure of a specified component is linear with composition.

"Regular" systems are defined as those in which the components form ideal solutions and whose vapors have equal gas law deviations. These are fairly common, and Raoult's law applies to them. Combining Raoult's law with Dalton's law of partial pressures, one may write

$$\pi y = Px \qquad (1)$$

where:

π = total pressure

P = vapor pressure of the specified component at the equilibrium temperature

y = mol fraction of the component in the vapor phase

x = mol fraction of the component in the liquid phase.

For components forming nonideal solutions but having negligible gas law deviations, thermodynamics shows that a relation of the type-form of Raoult's law may be applied if activities are used instead of ordinary concentrations. Activities are most simply defined as effective concentrations of such nature that when they are substituted into thermodynamic expressions in place of concentrations, the equations apply over the entire range of concentrations.

For any nonideal solution, the ratio of the activity of a component to its mol fraction differs from unity by an amount equal to that by which its actual partial pressure deviates from that required by Raoult's law (28). This ratio is commonly called the activity coefficient of the component, or for the special case under consideration, the Raoult's law deviation factor. It follows from the above considerations that Eq. (1) may be expressed exactly as

$$\pi y = P \underline{a} = P (x \gamma)$$

or more conveniently as

$$\gamma = \pi y / Px \qquad (2)$$

where:

$\underline{a}$ = activity

γ = activity coefficient or Raoult's law deviation factor

It is to be remembered that the condition of negligible deviation of the vapors from ideality restricts the applicability of Eq. (2).

In many cases this condition is not fulfilled, and for thermodynamic exactness, suitable corrections must be made for gas law deviations and pressure effects on the liquid phases. Benedict (1) has used the equation of state

$$PV = RT + BP \tag{3}$$

to correct for relatively small gas law deviations, liquid pressure effects and small volume changes on mixing, obtaining the following expression for calculating corrected or "thermodynamic" activity coefficients:

$$\log \gamma'_1 = \log \pi y_1 / P_1 x_1 - (\pi - P_1)(v_1 - B_1) / (2.303\ RT) \tag{4}$$

or more concisely,

$$\gamma'_1 = (\pi y_1)(Z_1) / (P_1 x_1) \tag{5}$$

where:

$$\log Z_1 = (P_1 - \pi)(V_1 - B_1) / (2.303\ RT)$$

v_1 = liquid specific volume of pure component 1, cc / mol

B_1 = second virial coefficient of pure component 1 in Eq. (3)

P_1 = vapor pressure of pure component 1 at the equilibrium temperature

T = temperature, ^{o}K.

R = gas constant

Z = correction factor for vapor nonideality and pressure effects on liquid phase

The value of the second virial coefficient in the above simplified equation of state may be calculated, (1) from a more rigorous equation of state for the pure component, (2) from compressibility factors, or (3) from the theorem of corresponding states utilizing critical constants (27).

Solutions to Gibbs-Duhem Equation

In the thermodynamic treatment of solutions, the concept of the partial molar quantity is of great importance. From its definition and the summation law, there can be derived expressions relating the changes of any extensive property of a system to changes in composition at constant temperature and pressure. Of immediate interest is the Gibbs expression for the relation between the partial molar free energies $\overline{G}_1$, $\overline{G}_2$ ....etc. of a system composed of components 1, 2, ... at constant temperature and pressure:

$$x_1 \left(\frac{\partial \overline{G}_1}{\partial x_1}\right)_{P,\,T} + x_2 \left(\frac{\partial \overline{G}_2}{\partial x_1}\right)_{P,\,T} + \ldots = 0 \qquad (6)$$

Under the special condition where the vapors follow the ideal gas law, one may write for constant temperature,

$$d\overline{G} = RT\ d \ln p \qquad (7)$$

In the general case, an exact and thermodynamically sound expression may be obtained by using fugacities instead of pressures so that Eq. (7) reads

$$d\overline{G} = RT \; d \ln f \tag{8}$$

Upon substitution of Eq. (8) into the Gibbs expression, one obtains the Gibbs-Duhem equation:

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right)_{P,T} + x_2 \left(\frac{\partial \ln f_2}{\partial x_1} \right) + \ldots = 0 \tag{9}$$

Eq. (9) can be transformed into a more useful form in terms of activity coefficients. Employing the definition of the activity or relative fugacity of Lewis and Randall (24), one may substitute for the fugacity its equivalent expression in mol fraction and activity coefficient, thus:

$$a_i = \gamma_i x_i = f_i / f_i^o \tag{10}$$

where f_i^o is the fugacity of the pure liquid.

Noting that the values of f_i^o are constant at constant temperature, that $x_i \; d \ln x_i = d x_i$, and that $d (x_1 + x_2 + x_3 + \ldots) = d (1) = 0$, one obtains,

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{P,T} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{P,T} + \ldots = 0 \tag{11}$$

For binary systems, since $x_1 = (1 - x_2)$, $d x_1 = - d x_2$, Eq. (11) simplifies to the symmetrical expression:

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{P,T} = x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{P,T} \quad (12)$$

Eq. (12) is of immediate value in evaluating the consistency of experimental vapor-liquid equilibrium data by relating the slopes of the activity coefficient-composition curves. But allowance must be made for the fact that such slopes are difficult to determine precisely.

The earliest attempts to obtain useful analytical solutions to Eq. (12) were made by Margules (25) and later by van Laar (40). With slight revisions, Carlson and Colburn (5), present the following equations as the Margules and van Laar solutions:

Margules

$$\log \gamma_1 = (2B - A)\, x_2^2 + 2(A - B)\, x_2^3 \quad (13)$$

$$\log \gamma_2 = (2A - B)\, x_1^2 + 2(B - A)\, x_1^3 \quad (14)$$

van Laar

$$\log \gamma_1 = \frac{A}{(1 + A\, x_1 / B\, x_2)^2} \quad (15)$$

$$\log \gamma_2 = \frac{B}{(1 + B\, x_2 / A\, x_1)^2} \quad (16)$$

where:

$$A = \log \gamma_1 \text{ at } x_1 = 0$$

$$B = \log \gamma_2 \text{ at } x_2 = 0$$

Ternary Equations

The many semi-theoretical "thermodynamic" correlations of binary and ternary liquid systems have been compared and systematized by Wohl (41) in a manner such that the relationships between the

numerous equations proposed are clearly shown so their relative merits may now be evaluated. Useful variations of the proposed equations in readily applicable forms are also given.

In accordance with Wohl's procedure, consider the total free energy content of any homogeneous system. This total free energy G_T may be expressed as follows:

$$G_T = \sum_1^n N_i G_i^\circ + \sum_1^n N_i RT \ln x_i + \sum_1^n N_i (\Delta G) \qquad (17)$$

where:

G_i° = free energy of one mol of pure component $\underline{i}$

N_i = number of mols of component $\underline{i}$

x_i = mol fraction of component $\underline{i}$

$$\sum_1^n N_i G_i^\circ = N_1 G_1^\circ + N_2 G_2^\circ + N_3 G_3^\circ + \cdots\cdots$$

$$\sum_1^n N_i RT \ln x_i = N_1 RT \ln x_1 + N_2 RT \ln x_2 + \cdots\cdots$$

ΔG = nonideality term

The nonideality term represents the difference between the free energy of one mol of a real mixture and a mixture of identical composition if it were ideal. This term has been designated by Scatchard and Hamer (36) as the excess free energy of the solution.

One may write an analogous expression to Eq. (17) in terms of activities or their equivalents, the mol fraction-activity coefficient products:

$$G_T = \sum N_i G_i^o + \sum N_i RT \ln x_i + \sum N_i RT \ln \gamma_i \qquad (18)$$

The partial free energy of any component may be obtained by performing the partial differentiation of the total free energy expression with respect to that component, thus:

$$\frac{\partial G_T}{\partial N_1} = G_1^o + \frac{\partial \sum N_i RT \ln x_i}{\partial N_1} + \frac{\partial \sum N_i (\Delta G)}{\partial N_1} \qquad (19)$$

Also,

$$\frac{\partial G_T}{\partial N_1} = G_1^o + \frac{\partial \sum N_i RT \ln x_i}{\partial N_1} + \frac{\partial \sum N_i RT \ln \gamma_i}{\partial N_1} \qquad (20)$$

Considering the principle expressed by Eq. (6) and the equation for the free energy in terms of activities, one may write,

$$x_1 \, d \ln a_1 + x_2 \, d \ln a_2 + x_3 \, d \ln a_3 + \ldots = 0 \qquad (21)$$

This may be written in terms of mol fractions and the respective activity coefficients as:

$$x_1 \, d \ln x_1 + x_1 \, d \ln \gamma_1 + x_2 \, d \ln x_2 + x_2 \, d \ln \gamma_2 + x_3 \, d \ln x_3 + x_3 \, d \ln \gamma_3 + \ldots = 0 \qquad (22)$$

Remembering that $x_i \, d \ln x_i = d x_i$, and that $d (x_1 + x_2 + \ldots) = d (1) = 0$, it follows that

$$x_1 \, d \ln x_1 + x_2 \, d \ln x_2 + x_3 \, d \ln x_3 + \ldots = 0 \qquad (23)$$

and therefore

$$x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 + x_3 d \ln \gamma_3 + \ldots = 0 \qquad (24)$$

The last term in Eq. (20) may then be evaluated to yield

$$\frac{\partial \sum N_i RT \ln \gamma_i}{\partial N_1} = RT \ln \gamma_1 \qquad (25)$$

It is seen that

$$RT \ln \gamma_1 = \frac{\partial (N_1 + N_2 + N_3 + \ldots) \Delta G}{\partial N_1} \qquad (26)$$

or

$$\ln \gamma_1 = \frac{\partial (N_1 + N_2 + N_3 + \ldots) \Delta G/RT}{\partial N_1} \qquad (27)$$

and in general terms

$$\ln \gamma_i = \frac{\partial (N_1 + N_2 + N_3 + \ldots) \Delta G/RT}{\partial N_i} \qquad (28)$$

With the aid of this fundamental equation and the various empirical equations for expressing the non-ideality factor $\Delta G/RT$ in terms of concentrations, Wohl (41) has systematically derived thermodynamically sound and readily applicable equations for binary and ternary systems.

Hougen and Watson (20) have presented a mathematical analysis of Wohl's technique, giving in detail the necessary steps whereby the equations of Margules and van Laar may be obtained, and also showing the

relation between these solutions and those obtained by Scatchard and co-workers (35, 37).

The general method may be extended to a system of any number of components. For deriving the so-called ternary three-suffix Margules equations, one may write an expression for the non-ideality factor according to the procedure of Scatchard and Prentiss (37) and as presented by Wohl (41):

$$\frac{\Delta G}{2.303\ RT} = x_1 x_2 2a_{12} + x_1 x_3 2a_{13} + x_2 x_3 2a_{23} + x_1^2 x_2 3a_{112} + x_1 x_2^2 3a_{122} + x_1^2 x_3 3a_{113} + x_1 x_3^2 3a_{133} + x_2^2 x_3 3a_{223} + x_2 x_3^2 3a_{233} + x_1 x_2 x_3 6a_{123} \qquad (29)$$

where the subscript of any "a" factor indicates that it appears in a term which contains the product of the mol fraction of the indicated components 1, 2, 3. An example would be a_{112} which would be a constant onto a term which contains the product $x_1^2 x_2$.

Introducing the following type of abbreviations,

$$2a_{12} + 3a_{122} = A_{1-2}\ ; \quad 2a_{12} + 3a_{112} = A_{2-1}$$

$$2a_{13} + 3a_{133} = A_{1-3}\ ; \quad 2a_{13} + 3a_{113} = A_{3-1} \qquad (30)$$

$$2a_{23} + 3a_{233} = A_{2-3}\ ; \quad 2a_{23} + 3a_{223} = A_{3-2}$$

and

$$3a_{112} + 3a_{133} + 3a_{223} - 6a_{123} = C \qquad (31)$$

there may be obtained the equivalent expression for Eq. (29)

$$\frac{\Delta G}{2.303\,RT} = x_1 x_2 (x_1 A_{2-1} + x_2 A_{1-2}) + x_1 x_3 (x_1 A_{3-1} + x_3 A_{1-3}) + x_2 x_3 (x_2 A_{3-2} + x_3 A_{2-3}) + x_1 x_2 x_3 (A_{2-1} + A_{1-3} + A_{3-2} - C) \quad (32)$$

By successive application of Eq. (28) and performing the indicated operation, there may be obtained the following set of equations:

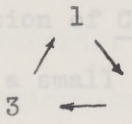
$$\log \gamma_1 = x_2^2 [A_{1-2} + 2x_1 (A_{2-1} - A_{1-2})] + x_3^2 [A_{1-3} + 2x_1 (A_{3-1} - A_{1-3})] + x_2 x_3 [A_{2-1} + A_{1-3} - A_{3-2} + 2x_1 (A_{3-1} - A_{1-3}) + 2x_3 (A_{3-2} - A_{2-3}) - C (1-2x_1)] \quad (33)$$

$$\log \gamma_2 = x_3^2 [A_{2-3} + 2x_2 (A_{3-2} - A_{2-3})] + x_1^2 [A_{2-1} + 2x_2 (A_{1-2} - A_{2-1})] + x_1 x_3 [A_{3-2} + A_{2-1} - A_{1-3} + 2x_2 (A_{1-2} - A_{2-1}) + 2x_1 (A_{1-3} - A_{3-1}) - C (1-2x_2)] \quad (34)$$

$$\log \gamma_3 = x_1^2 [A_{3-1} + 2x_3 (A_{1-3} - A_{3-1})] + x_2^2 [A_{3-2} + 2x_3 (A_{2-3} - A_{3-2})] + x_1 x_2 [A_{1-3} + A_{3-2} - A_{2-1} + 2x_3 (A_{2-3} - A_{3-2}) + 2x_2 (A_{2-1} - A_{1-2}) - C (1-2x_3)] \quad (35)$$

Since the above equations are symmetrical between the 3 components, the equation for $\log \gamma_2$ could have been written at once from that of $\log \gamma_1$ by using the "rotation principle" on the subscripts. In order to obtain the expression for $\log \gamma_2$ from that of $\log \gamma_1$, one merely

has to advance in the subscript triangle



one step in the indicated direction. The equation for log γ_3 may be obtained similarly from that of log γ_2.

In these equations, the terms A_{1-2}, A_{2-1}, etc. represent the end values (where x = 0) of the logarithms of the activity coefficients in the binary systems indicated by the subscripts, namely:

$$\begin{aligned}
&\text{limit log } \gamma_1 \quad (x_1 \longrightarrow 0,\ x_2 \longrightarrow 1) = A_{1-2} \\
&\text{limit log } \gamma_2 \quad (x_2 \longrightarrow 0,\ x_1 \longrightarrow 1) = A_{2-1} \\
&\text{limit log } \gamma_1 \quad (x_1 \longrightarrow 0,\ x_3 \longrightarrow 1) = A_{1-3} \\
&\text{limit log } \gamma_3 \quad (x_3 \longrightarrow 0,\ x_1 \longrightarrow 1) = A_{3-1} \\
&\text{limit log } \gamma_2 \quad (x_2 \longrightarrow 0,\ x_3 \longrightarrow 1) = A_{2-3} \\
&\text{limit log } \gamma_3 \quad (x_3 \longrightarrow 0,\ x_2 \longrightarrow 1) = A_{3-2}
\end{aligned} \tag{36}$$

Consideration of Eqs. (33), (34), and (35) shows that the description of a ternary system requires evaluation of six independent binary constants from the three binary systems involved, plus one ternary constant C. For Eq. (33), the ternary constant has its greatest influence on the value of log γ_1 when the term $x_2 x_3(1 - 2x_1)$ is at its maximum value, which occurs when x_1 is very small and x_2 is equal to x_3. It is apparent that the C term vanishes where x_1 is equal to 0.50 and reverses

its sign at high values of x_1. Similarly for $\log \gamma_2$ and $\log \gamma_3$ in Eqs. (34) and (35).

For experimental evaluation of C, the composition of the most suitable mixture is seen to be a small concentration of one component and approximately equal concentrations for the remaining two.

Azeotropism

Ewell and Berg (11) attribute deviations from ideality of solutions to the effects of residual hydrogen bonds and internal pressure, the former being the more influential. The concept of hydrogen bonding is that an active hydrogen atom can coordinate between two molecules of oxygen, nitrogen, or fluorine. It can also coordinate between any one of these donor atoms and a carbon atom, provided a sufficient number of negative groups or atoms are attached to the carbon atom.

The strength of the hydrogen coordination bond depends upon the nature of the atoms between which the hydrogen is coordinating. The occurrence of a constant boiling mixture depends equally on the two factors, difference in boiling points between the pure components, and the extent of nonideality of the solution.

Deviations from ideality of the solution are present when there are volume changes and heat effects upon mixing the components of a solution. For those systems which have vapor pressures larger than required by Raoult's law, there will be absorption of heat upon mixing. Such systems form minimum-boiling azeotropes when the boiling points of the pure components are sufficiently close. For those components which form maximum-boiling azeotropes there will be an evolution of heat upon mixing.

Since minimum-boiling azeotropes require positive deviations from Raoult's law, the activity coefficients will be greater than unity, and necessarily so for both components. Correspondingly, the activity coefficients of components of maximum-boiling azeotropes must be less than unity.

Heats of Solution — Heats of solution can be most accurately evaluated by calculation from the change of activity coefficients with temperature where adequate data are available. The relation is,

$$\frac{d \log \gamma'}{d\,(1/T)} = \frac{\bar{L}}{2.303\,R}$$

where:

$\bar{L}$ = partial molal heat of solution.

The activity coefficients so calculated must be obtained from activity coefficients which have been corrected for gas law deviations. This is necessary because small discrepancies in the activity coefficients magnify in the calculated heats of solution.

By plotting $\log \gamma'$ vs. $(1/T)$, the partial molal heats of solution may be calculated from the slope of the curve. Integral heats of solution may be obtained from the partial values by graphical integration.

III

SUMMARY OF RESULTS

Experimental — Isothermal vapor-liquid equilibrium data have been determined for the binary and ternary mixtures of acetone, methanol, and water. For the binary systems acetone-water and methanol-water, the data were obtained at temperature intervals of 50°C from 100°C to 250°C inclusive. Since 250°C is above the critical temperatures of both acetone and methanol, the highest temperature determinations on this binary were 200°C. Complete ternary data were determined at 100°C and 250°C. Selected ternary determinations were also obtained at 150°C and 200°C to evaluate the ternary constant C and enable estimation of vapor-liquid equilibria at these temperatures.

The 250°C isotherms were determined to establish the compositions which exist as single phase systems (with identical "vapor" and "liquid" compositions or phases). For the ternary this involved the establishment of the critical locus of mixtures which result in a single-phase at 250°C. The above is equivalent to saying that the compositions of aqueous binary and ternary mixtures were determined which have a critical temperature of 250°C.

The experimental isotherms are summarized below.

System	Temperature, °C
Acetone-Water	100°, 150°, 200°, 250°
Methanol-Water	100°, 150°, 200°, 250°
Acetone-Methanol	100°, 150°, 200°
Acetone-Methanol-Water	100°, 250°, plus selected points at 150°, 200°

Calculated Equilibrium Data

In addition to the experimental work on the acetone-methanol system, vapor-liquid values were calculated and compared with the experimental data at 150°C and 200°C. This was a necessary check because acetone apparently undergoes chemical changes at the higher temperatures at a rate sufficient to render some of the data incorrect.

Thermodynamic activity coefficients were calculated as isotherms for the binaries and the ternary up to and including 200°C. These were appropriately used to calculate vapor-liquid values suitable for correlation and extension of the binary results to those of the ternary. The binary and ternary equations of Margules as presented by Wohl (41) were chosen as optimum between comprehensiveness and ease of application. Ternary constants were evaluated from data at selected compositions. With the aid of the experimental aqueous binary data, those calculated for acetone-methanol, and the ternary diagrams at 100°C and 250°C, complete ternary diagrams could be estimated for the intermediate temperatures of 150°C and 200°C, and were so constructed.

Heats of Solution — The partial molal and integral heats of solution for acetone in water have been calculated from the changes in activity coefficients of acetone with temperature. For the other two binary systems, activity coefficients are substantially independent of temperature between 100° C and 200°C, from which it follows that heats of solution are negligible.

Plots — The experimental data are presented on y---x diagrams. Ternary results are plotted on standard triangular diagrams. Binary activity coefficients are plotted as log γ' vs. x to obtain the required end constants. Ternary activity coefficients are plotted in a similar manner by including parameters of the concentration of the third component for each point, in the manner of Colburn and Schoenborn (6). Calculated ternary activity coefficient curves are included to show differences between calculated and experimental activity coefficients.

Z- Correction Factors — Activity coefficient correction factors accounting for nonideality of the vapors and the effects of pressure on the liquid phases have been calculated. Compressibility factors were used to compute the required second virial coefficients in the equation of state applied to the various components.

Analytical Data — Analytical data for the binary and ternary systems determined by Griswold and Buford (15) are used in this work. Experimental rechecking of the data and comparison with data reported in the literature proved their reliability and consistency.

IV

RESULTS AND CONCLUSIONS

Z-Correction Factors

Thermodynamic activity coefficients were calculated from the experimental data using Eq. (5) containing the correction factor Z. It may be recalled that the expression for Z assumed the form:

$$\log Z_1 = (P_1 - \pi)(v_1 - B_1)/(2.303\ RT) \qquad (38)$$

A literature search revealed that the only data suitable for calculating the second virial coefficient B for acetone and for methanol were those reported by Eucken and Meyer (10). These data are for pressures below atmospheric and not applicable to present conditions. As the next best alternative, the second virial coefficients were calculated from compressibility factors using the relation

$$B_i = V_i\ (u - 1)$$

where:

B_i = second virial coefficient for component i

V_i = ideal volume calculated by PV = RT

u = compressibility factor

The compressibility factors were read from charts prepared by Hougen and Watson (21) at each temperature and a series of pressures. The liquid specific volumes v, vapor pressures, and critical temperatures

for acetone and methanol used were taken from the International Critical Tables (22). Corresponding values for water were taken from handbook compilations (17).

For each isotherm on each component, a sufficient number of points were calculated to reliably establish the Z curve. A slight curvature was found in some of the Z curves. The calculated values of Z for each component were plotted against total pressures at constant temperatures. These plots permitted quick determination of any Z factor at the total equilibrium pressure of a run. The data for the correction factors are given in Tables XXIII, XXIV, and XXV.

Mixture Criticals

At 250°C the vapor-liquid equilibrium curves become discontinuous at compositions whose critical temperature is 250°C. These are shown both on the y--x plots and the ternary diagram. The critical mixtures were determined and confirmed by experimental points on both sides of the critical. Analyses showed also that samples from liquid and vapor condensate chambers of the equilibrium still had the same composition when on the critical border curve. Further proof was obtained by the observation that relatively large changes in temperature only caused small changes in pressures, in contradistinction to correspondingly large pressure changes with temperature whenever the system is definitely two-phase. Just above the critical condition, the system shows the pressure-temperature behavior of a gas, while just below the critical condition, it shows a vapor pressure-temperature behavior, the latter being much the more sensitive to temperature changes.

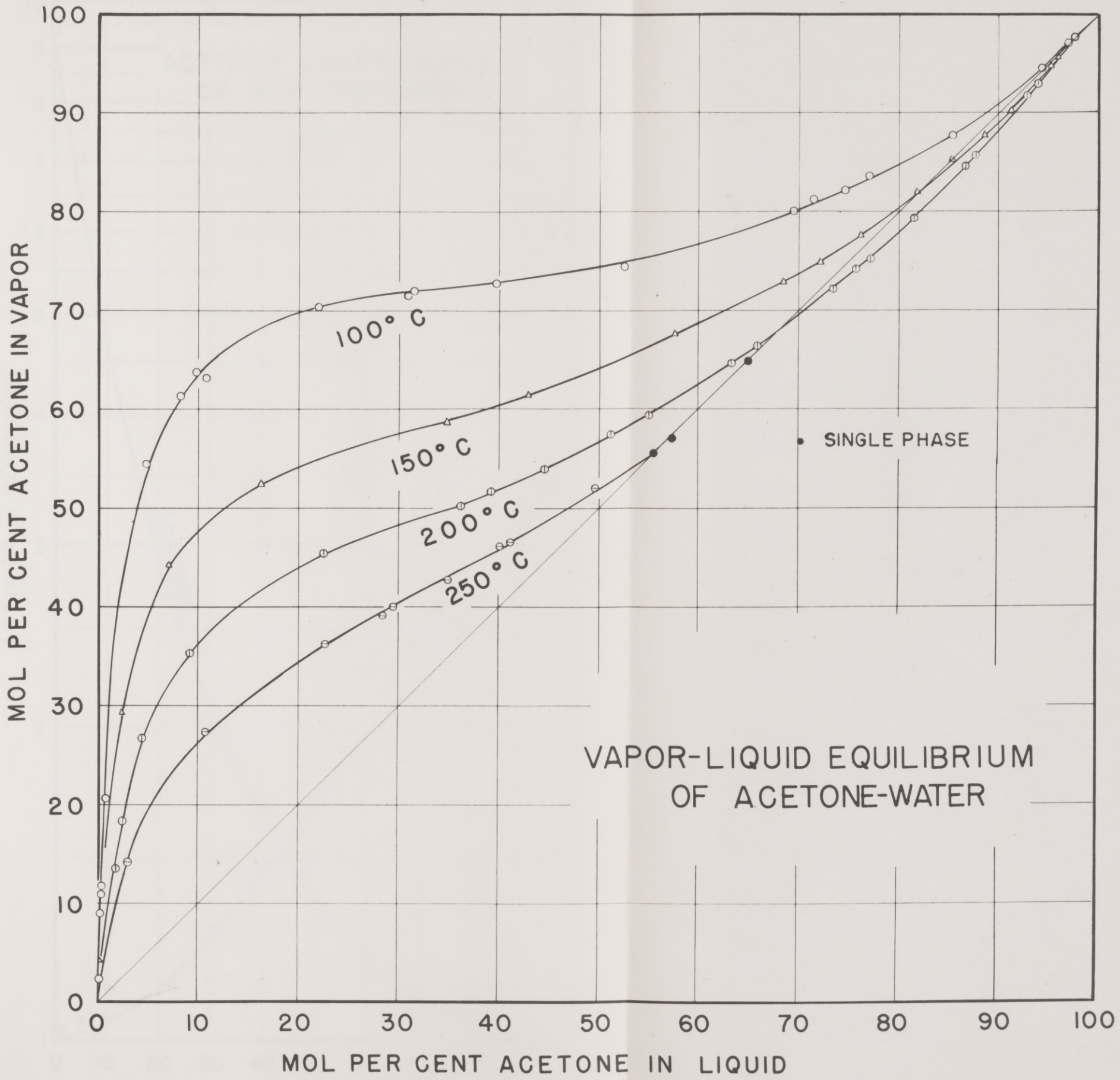

MOL PER CENT ACETONE IN VAPOR
MOL PER CENT ACETONE IN LIQUID
0
10
20
30
40
50
60
70
80
90
100
100° C
150° C
200° C
250° C
SINGLE PHASE
VAPOR-LIQUID EQUILIBRIUM
OF ACETONE-WATER

FIGURE 1

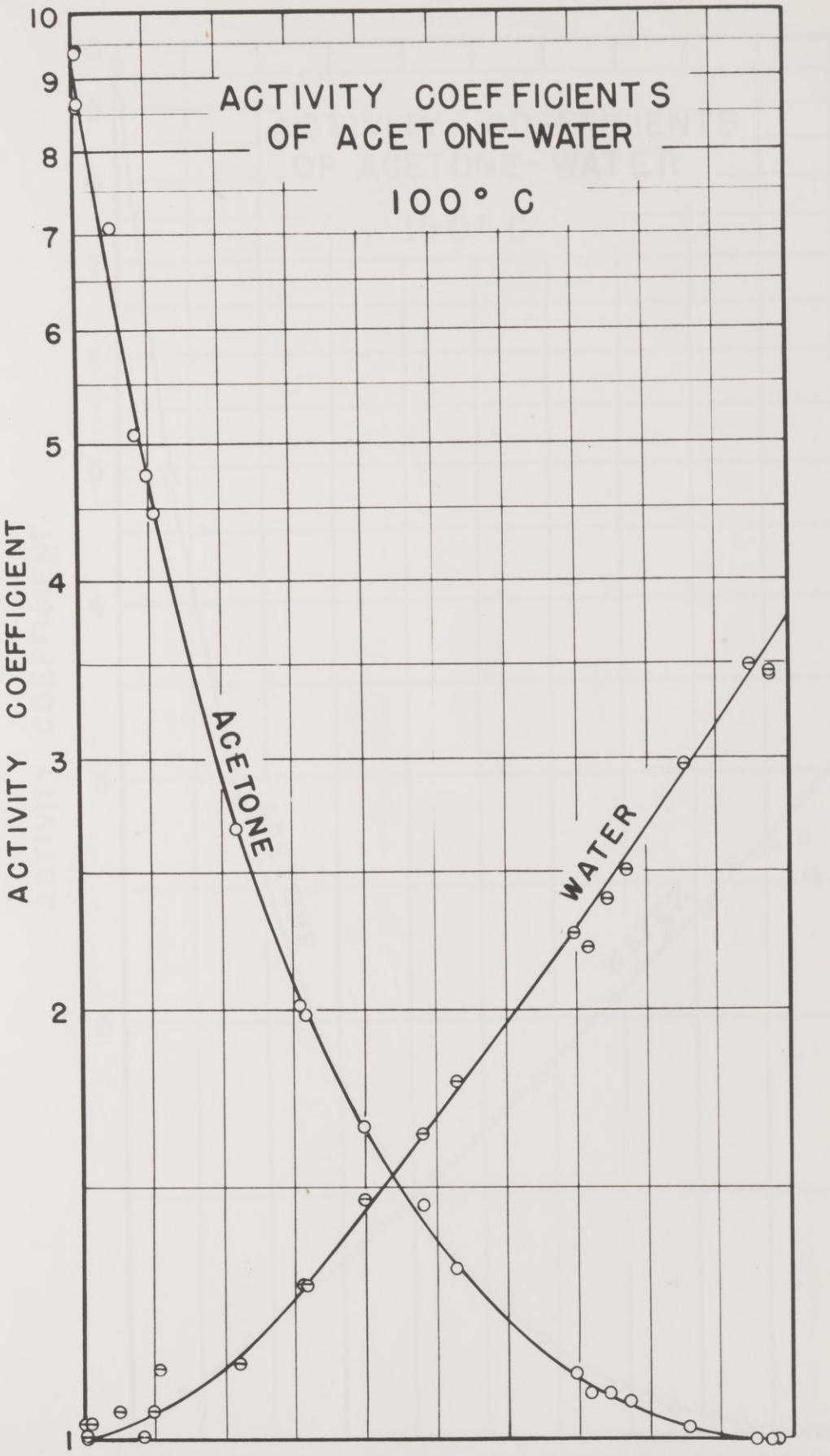

ACTIVITY COEFFICIENTS
OF ACETONE-WATER
100° C
ACTIVITY COEFFICIENT
ACETONE
WATER
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT ACETONE IN LIQUID

FIGURE 2

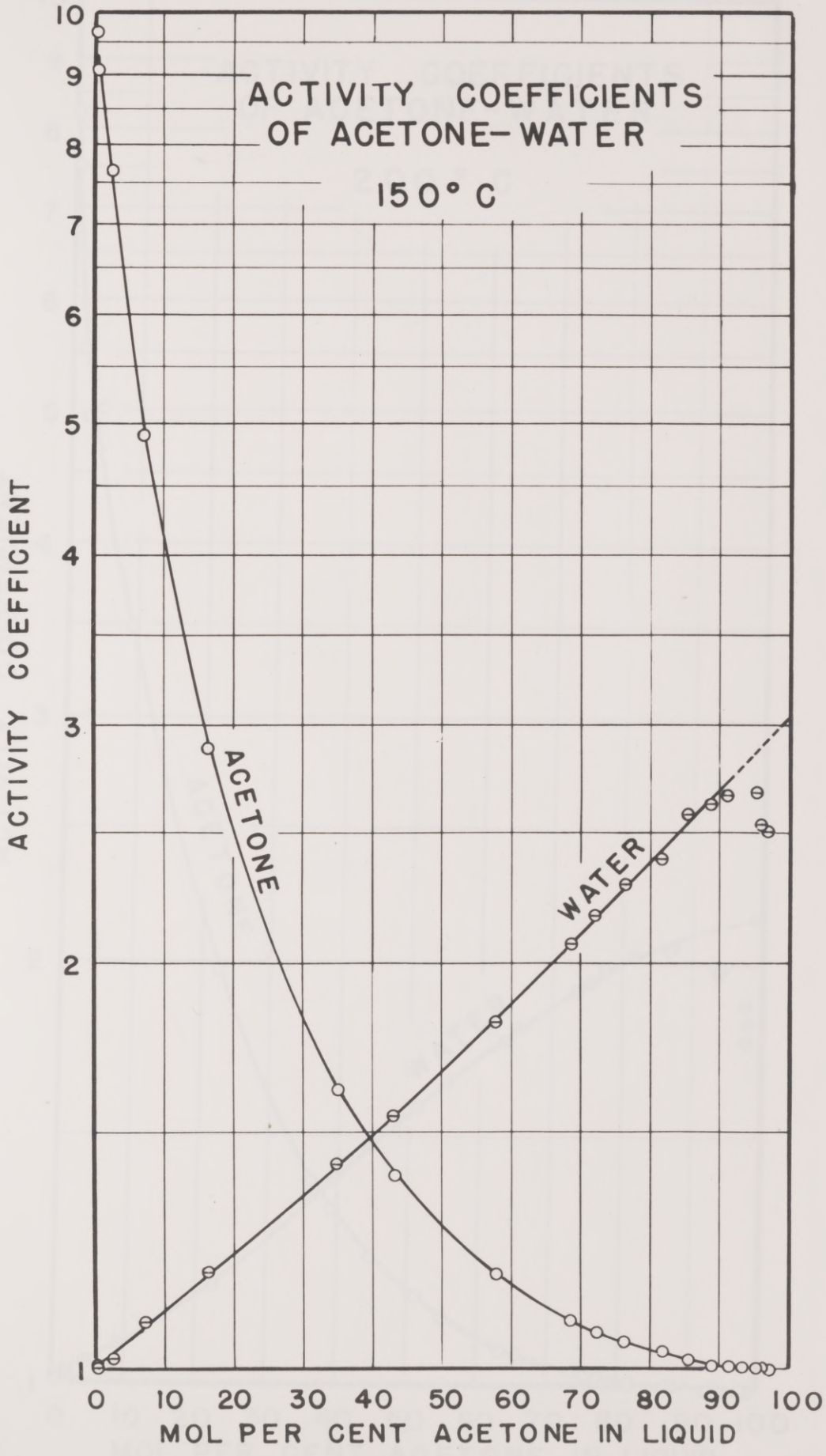

ACTIVITY COEFFICIENTS
OF ACETONE-WATER
150° C
ACTIVITY COEFFICIENT
ACETONE
WATER
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT ACETONE IN LIQUID

FIGURE 3

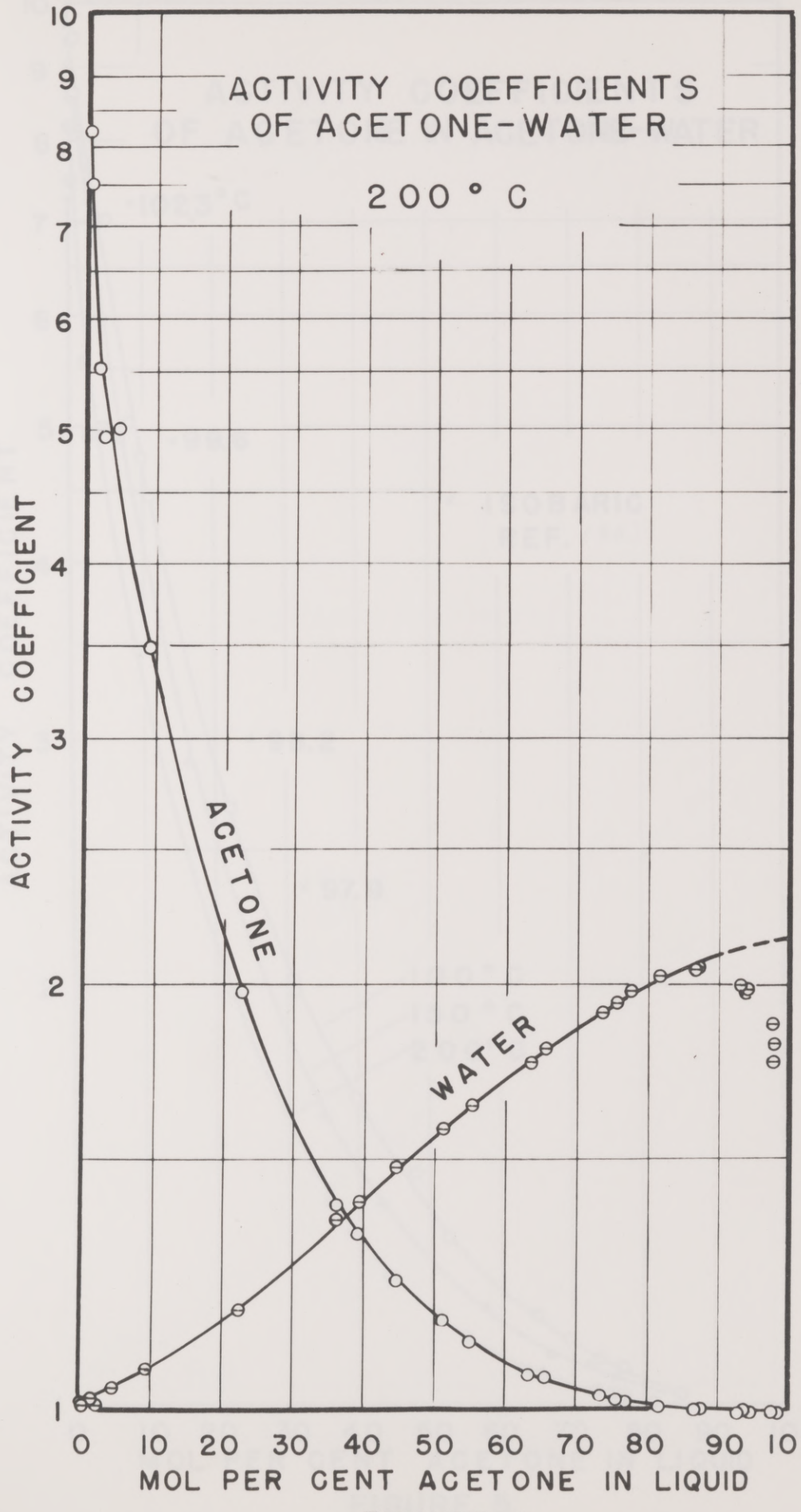

ACTIVITY COEFFICIENTS
OF ACETONE-WATER
200° C
ACTIVITY COEFFICIENT
10
9
8
7
6
5
4
3
2
1
ACETONE
WATER
0 10 20 30 40 50 60 70 80 90 100
MOL PER CENT ACETONE IN LIQUID

FIGURE 4

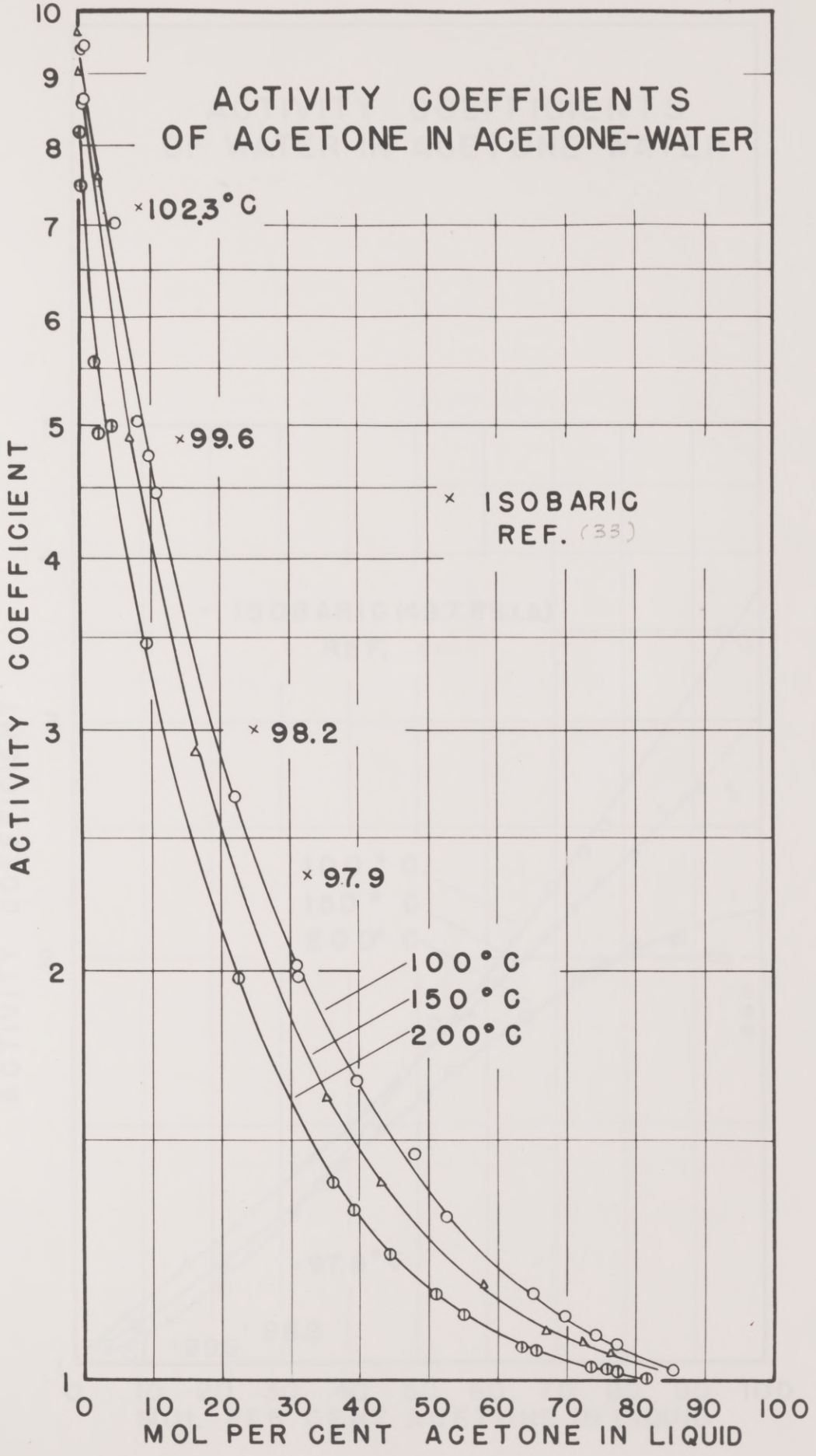

ACTIVITY COEFFICIENTS
OF ACETONE IN ACETONE-WATER
×102.3°C
×99.6
× ISOBARIC
REF. (33)
×98.2
×97.9
100°C
150°C
200°C
ACTIVITY COEFFICIENT
MOL PER CENT ACETONE IN LIQUID
0 10 20 30 40 50 60 70 80 90 100
1 2 3 4 5 6 7 8 9 10

FIGURE 5

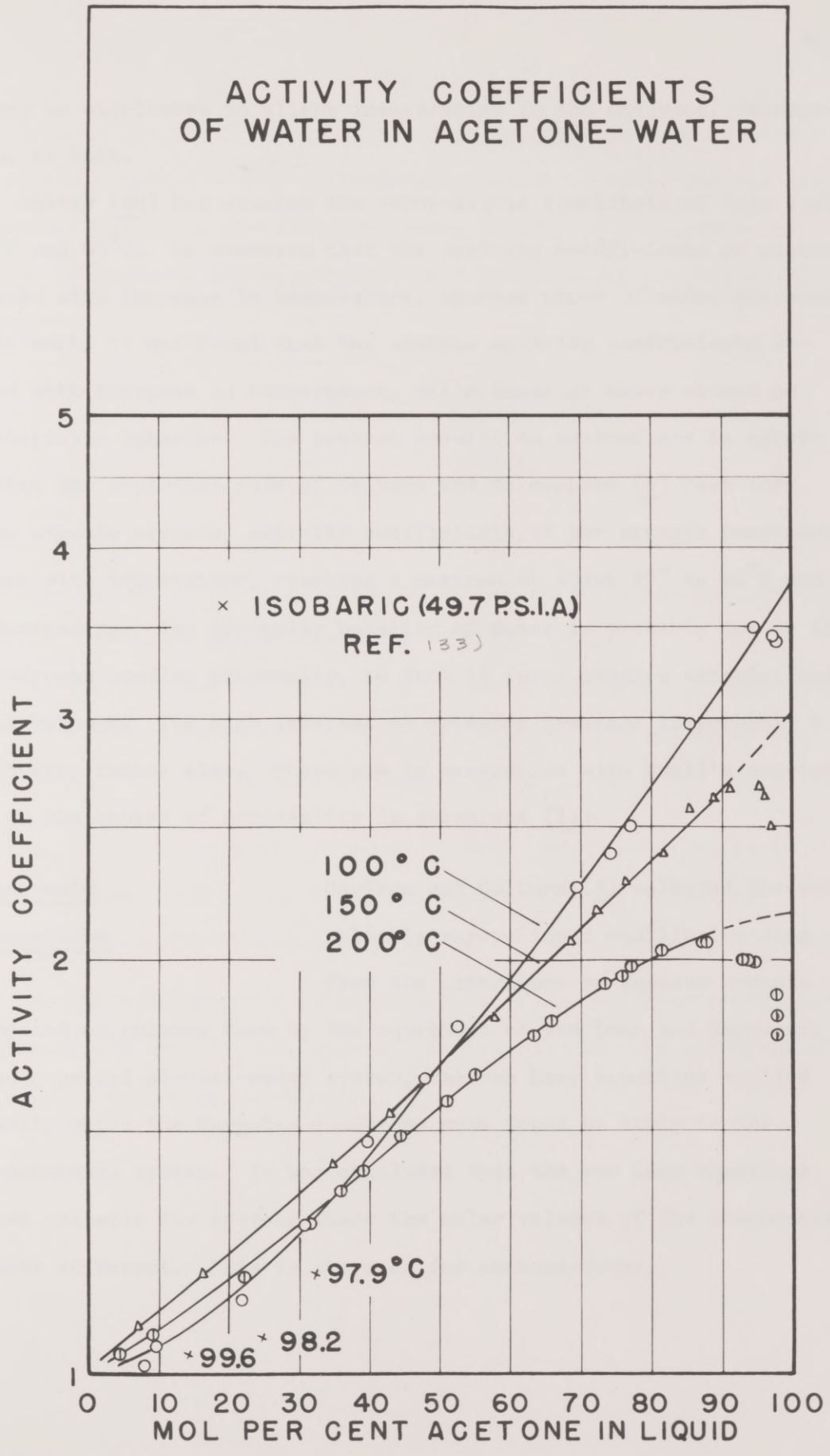

ACTIVITY COEFFICIENTS
OF WATER IN ACETONE-WATER
ACTIVITY COEFFICIENT
5
4
3
2
1
× ISOBARIC (49.7 P.S.I.A.)
REF. 133)
100° C
150° C
200° C
×97.9°C
×99.6
×98.2
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT ACETONE IN LIQUID

FIGURE 6

This may be attributed to slight inaccuracies in the analyses, decomposition, or both.

Soltes (38) has studied the vapor-liquid equilibria of this system at 45°C and 60°C. He observed that the activity coefficients of acetone increased with increase in temperature, whereas those of water decreased. In this work, it was found that the acetone activity coefficients decreased with increase in temperature, while those of water showed no characteristic behavior. The present results on acetone are in agreement with the empirical rule of Colburn and Schoenborn (6) that for aqueous organic systems, activity coefficients of the organic components increase with temperature, reaching a maximum at about 50° to 80°C and then decreasing. The irregular behavior of water is probably due to its high hydrogen bonding propensity, so that it forms complex associations in such systems. Its high internal or cohesive pressure is probably a contributing factor also. These are in accordance with Ewell's considerations on the causes of nonideality in solutions (11).

Thermodynamic Considerations

Carlson and Colburn (5) selected the most reliable vapor-liquid equilibrium data from the literature on aqueous organic systems and correlated them by the equations of van Laar and Margules. For the n-propyl alcohol-water system, the van Laar equations applied very well, while the Margules equations were found to apply to the water-n-butanol system. It was concluded that the van Laar equations are most suitable for systems where the molar volumes of the components are quite different. This is the case for acetone-water.

A rapid qualitative test of the data is afforded by considerations at the midpoint of the activity coefficient curves. The van Laar and Margules solutions yield the following relationships between the activity coefficients at the midpoint (x = 0.5) and the end values of the curves:

$$\frac{\log \gamma'_1}{A_{3-1}} = \frac{\log \gamma'_3}{A_{1-3}} = \frac{(A_{1-3})(A_{3-1})}{(A_{1-3} + A_{3-1})^2} \qquad (40)$$

where the subscripts 1 and 3 refer, respectively, to acetone and water. The A terms represent the end constants of the activity coefficient-composition curves as defined previously by Eq. (36).

For the Margules solutions, the ratios of the activity coefficients to the end constants are equal to 1/4 regardless of the values of the end constants. In the van Laar solutions, if $A_{1-3} = A_{3-1}$ the ratio $(A_{1-3})(A_{3-1}) / (A_{1-3} + A_{3-1})^2$ is equal to 1/4. As the end constants diverge from each other, this ratio decreases slightly; e.g., when $A_{1-3} = 2A_{3-1}$ the ratio is equal to 2/9.

The end constants and midpoint values of the activity coefficients are summarized below for this system. It is seen that the agreement with the predicted values is excellent.

Midpoint Relations Between Activity Coefficients and End Constants (Acetone-Water)

Temp., °C	γ'_1 ($x_1 = 0$)	γ'_3 ($x_3 = 0$)	A_{1-3}	A_{3-1}	A_{1-3}/A_{3-1}
100	9.250	3.781	0.9661	0.5776	1.671
150	9.250	3.035	0.9661	0.4822	2.00
200	8.210	2.170	0.9143	0.3365	2.715

At x = 0.50

Temp., C	γ'_1	γ'_3	log γ'_1	log γ'_3
100	1.375	1.690	0.1383	0.2279
150	1.273	1.660	0.1048	0.2201
200	1.170	1.563	0.0682	0.1940

Temp., °C	log γ'_3/A_{1-3}	log γ'_1/A_{3-1}	$\frac{(A_{1-3})(A_{3-1})}{(A_{1-3} + A_{3-1})^2}$
100	0.238	0.239	0.234
150	0.228	0.217	0.222
200	0.212	0.203	0.197

Azeotropism — At atmospheric pressure no azeotrope occurs in the acetone-water system. Azeotropism does appear, however, at elevated temperatures. From the y--x plots, the experimentally determined minimum-boiling azeotropic compositions are,

100°C	Uncertain
150°C	81.8 mol per cent acetone
200°C	68.5 mol per cent acetone

The existence or non-existence of an azeotrope at 100° C is uncertain because the equilibrium curve approaches the 45° reference line tangentially in that region. At approximately 95 mol per cent acetone, the difference between vapor and liquid compositions is only about 0.20 mol per cent. Beyond that, a determination showed a difference of 0.10 mol per cent. In both cases more acetone was found in the vapor phase. The limits of accuracy of the density method of analysis are of the same order as these apparent differences.

No maximum in total pressure was observed in this region. Total pressures at equilibrium were found to be 53.4 to 53.5 psia, which is 0.4 to 0.5 lb. lower than the vapor pressure of acetone at 100°C.

Differences between vapor and liquid compositions and between equilibrium pressures and the vapor pressures are so slight in this restricted range of compositions that they are not conclusive for judging the behavior of the system. It may well be that at 100°C the system is on the threshold of azeotrope formation. If an azeotrope does exist, the

differences between vapor and liquid compositions on both sides of the azeotropic point are so small that they cannot be detected easily for definite proof.

Nutting and Horsley (29) found that straight lines are produced by plotting the logarithms of the vapor pressures of azeotropes against the reciprocals of ($T^{\circ}C$ + 230) after the method of Cox (9). From 100° to 200°C a similar plot yields a straight line for the vapor pressure of acetone, and one might reasonably expect this linear relationship to hold for the vapor pressures of acetone-water azeogropes.

Othmer and Morley (33) reported an azeotrope (apparently extrapolated) for this system at 49.7 psia and 95.8 °C containing 96.5 mol per cent acetone along with those actually determined at 124.0 °C and 155.8°C. The data of these investigators were plotted as described along with the present results. All agree within experimental accuracy except one reported value at 95.8°C, which was inconsistent with the other points. Considering this inconsistency and the contrary evidence of no maximum in the total pressure, the existence of an azeotrope at 95.8°C is questioned.

Comparison with Literature Data

Several points near 100°C were selected from the isobaric data of Othmer and Morley (33) for comparison with the present 100°C isotherm. Activity coefficients were calculated from the literature data and corrected for vapor nonideality and pressure effects on

the liquid. The results are plotted in Figures 5 and 6. The activity coefficients for acetone are higher and those for water are lower than the present values. The differences are too great to be ascribed to the differences in temperature.

One factor which is a source of disagreement is the analytical data used. Othmer and Morley used density data reported by Squibb (39) for their analyses. The density data used in this research were those determined by Griswold and Buford (15). The latter agreed with those determined by McElroy (26) which have been checked by York and Holmes (43). From about 20 mol per cent to about 90 mol per cent acetone, the difference between the data of Griswold-Buford-McElroy and Squibb averages about 1 mol per cent low in acetone on Squibb's data for a given density. The differences are greatest from about 25 mol per cent to about 50 mol per cent acetone, where the deviations amount to approximately 1.3 mol per cent. Squibb (39) admitted limitations in his results as he could not certify that the acetone used was completely anhydrous. No account was taken of the effect of vapor loss on mixing the acetone with water nor did he take precautions to avoid this source of error.

Correction of the vapor-liquid equilibrium data to the same analytical basis does not fully resolve the discrepancies noted. Inaccuracies in total pressure observations may be eliminated from consideration because such errors would affect activity coefficients of both components in the same direction. Erroneous temperature readings are also eliminated since they would also affect the activity coefficients in the same direction.

The remaining possibility is that the vapors are higher in acetone and lower in water than for true equilibrium. This condition occurs where there is enrichment of the vapor in the still after it disengages from the boiling liquid.

Although it is presumed that the Othmer still is constructed and operated so that the inner vapor tube eliminates the effects of refluxing, this is true only of the vapor after it enters the tube. The still construction does not prevent some of the vapor which has been enriched at the wall from entering the inner tube.

With no heater around the still's main body to compensate for heat loss, there is nothing to prevent the vapor in contact with the wall from condensing and refluxing down the wall. At moderate or low temperatures the effect may be insignificant due to the low temperature difference between the still wall and surrounding atmosphere, but at higher temperatures it cannot be neglected. Insulation alone will greatly reduce but cannot completely prevent heat losses and subsequent partial condensation of the vapor.

To be sure, the vapor surrounding the inner vapor tube prevents partial condensation and reflux action of the vapor after entering the tube. There is no vapor enrichment here. But because of partial condensation next to the wall, the vapors evolved are richer in the lower boiling component. There is no vapor enrichment in the vapor tube but the vapors entering the tube have been enriched by partial condensation action.

The use of an inert gas to control pressure is not considered good technique because it introduces an additional source of error.

Solubility of the gas in the liquid may be significant but it is not considered to be the major source of the error per se.

Consider the functioning of a still containing an inert gas along with the vapor. The cooled vapor condensate along with the dissolved gas flows into the reboiler where the temperature is much higher, and the dissolved gas comes out of solution. As it bubbles up through the liquid, it exerts a stripping action on the more volatile component, thus enriching the vapor. Solubility and condenser temperature determine how much gas is carried into the boiler per unit amount of return condensate. Condensate recycling, with respect to the dissolved gas, is equivalent to a continuous stripping action by the gas.

The discrepancies between this laboratory's results and those of Othmer and Morley are apparently due to the enrichment of the vapors by partial condensation and stripping action of the inert gas which were operative in the latter's equilibrium still.

Heats of Solution

The partial molal heats of solution for acetone in water were calculated from the thermodynamic activity coefficients of acetone at the several temperatures by Eq. (37), proceeding as previously noted. Heats of solution were calculated for the temperature intervals 100° to 150°C, 150° to 200°C, and 100° to 200°C. The activity coefficient-temperature curves are given in Figure 7. In evaluating the slopes of the log γ' vs. 1/T curves, straight lines were assumed between the noted

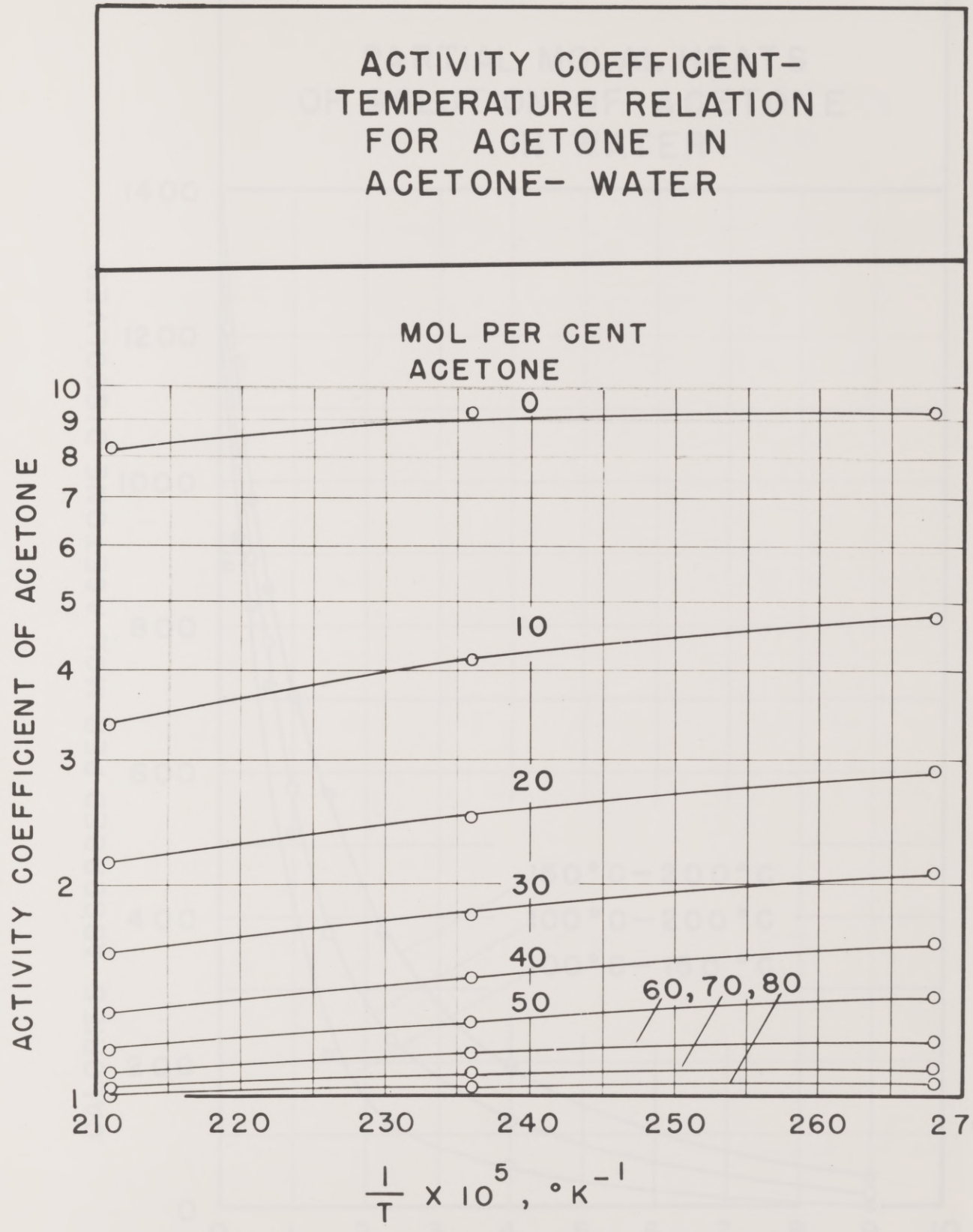

ACTIVITY COEFFICIENT-
TEMPERATURE RELATION
FOR ACETONE IN
ACETONE- WATER
MOL PER CENT
ACETONE
0
10
20
30
40
50
60,70,80
ACTIVITY COEFFICIENT OF ACETONE
10
9
8
7
6
5
4
3
2
1
210
220
230
240
250
260
270
1/T X 10^5, °K^-1

FIGURE 7

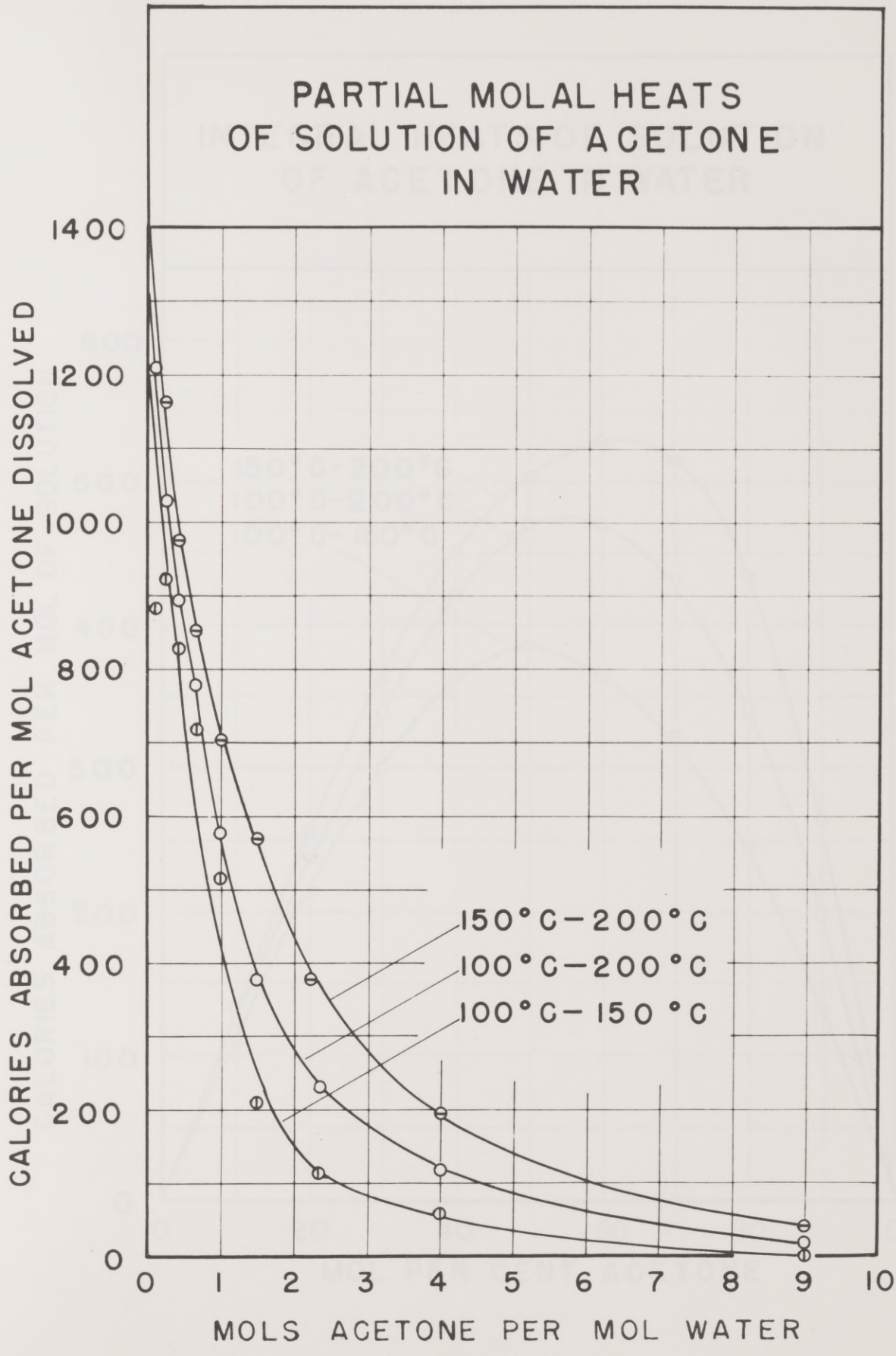

PARTIAL MOLAL HEATS
OF SOLUTION OF ACETONE
IN WATER
CALORIES ABSORBED PER MOL ACETONE DISSOLVED
1400
1200
1000
800
600
400
200
0
0
1
2
3
4
5
6
7
8
9
10
MOLS ACETONE PER MOL WATER
150°C–200°C
100°C–200°C
100°C–150°C

FIGURE 8

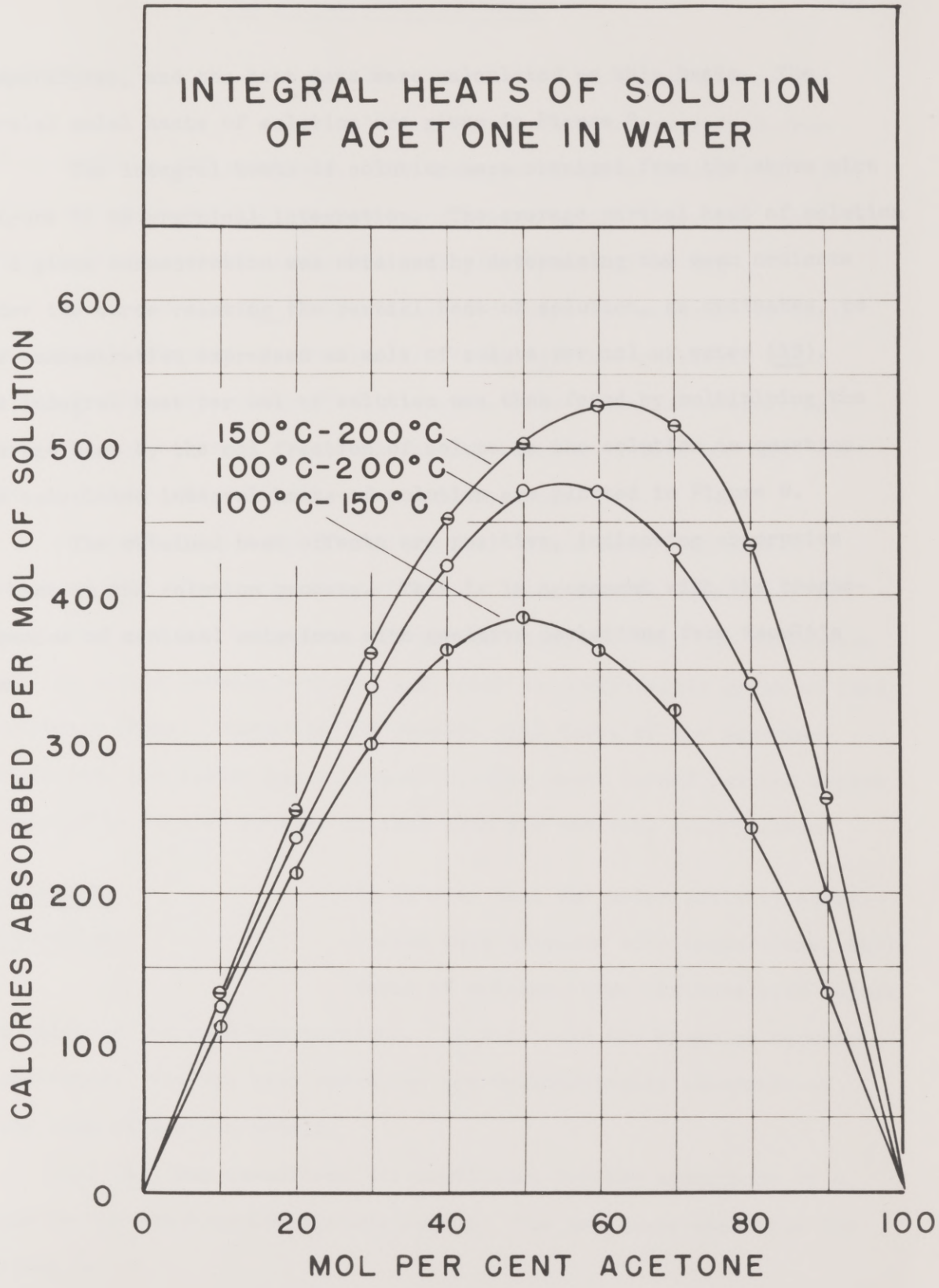

INTEGRAL HEATS OF SOLUTION
OF ACETONE IN WATER
CALORIES ABSORBED PER MOL OF SOLUTION
600
500
400
300
200
100
0
150°C-200°C
100°C-200°C
100°C-150°C
0
20
40
60
80
100
MOL PER CENT ACETONE

FIGURE 9

temperatures, and the heat data were calculated on this basis. The partial molal heats of solution are given in Figure 8.

The integral heats of solution were obtained from the above plot (Figure 8) by graphical integration. The average partial heat of solution at a given concentration was obtained by determining the mean ordinate under the curve relating the partial heat of solution, as ordinates, to the concentration expressed as mols of solute per mol of water (19). The integral heat per mol of solution was then found by multiplying the average heat by the mol fraction of solute in the solution in question. The calculated integral heats of solution are plotted in Figure 9.

The obtained heat effects are positive, indicating absorption of heat in the solution process. This is in agreement with the thermodynamics of nonideal solutions with positive deviations from Raoult's law.

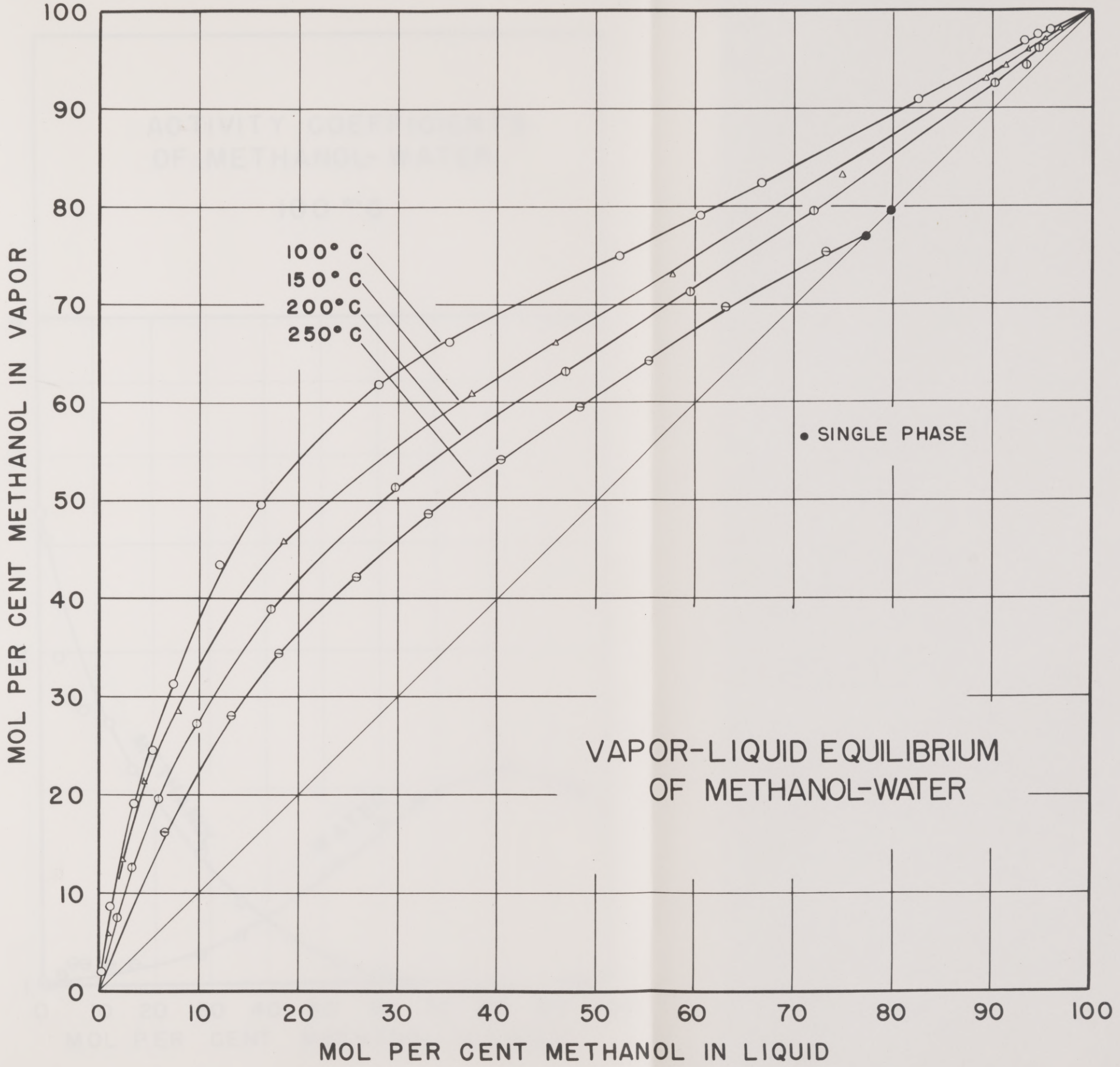

100° C
150° C
200° C
250° C
• SINGLE PHASE
VAPOR-LIQUID EQUILIBRIUM
OF METHANOL-WATER
MOL PER CENT METHANOL IN VAPOR
MOL PER CENT METHANOL IN LIQUID
0
10
20
30
40
50
60
70
80
90
100

FIGURE 10

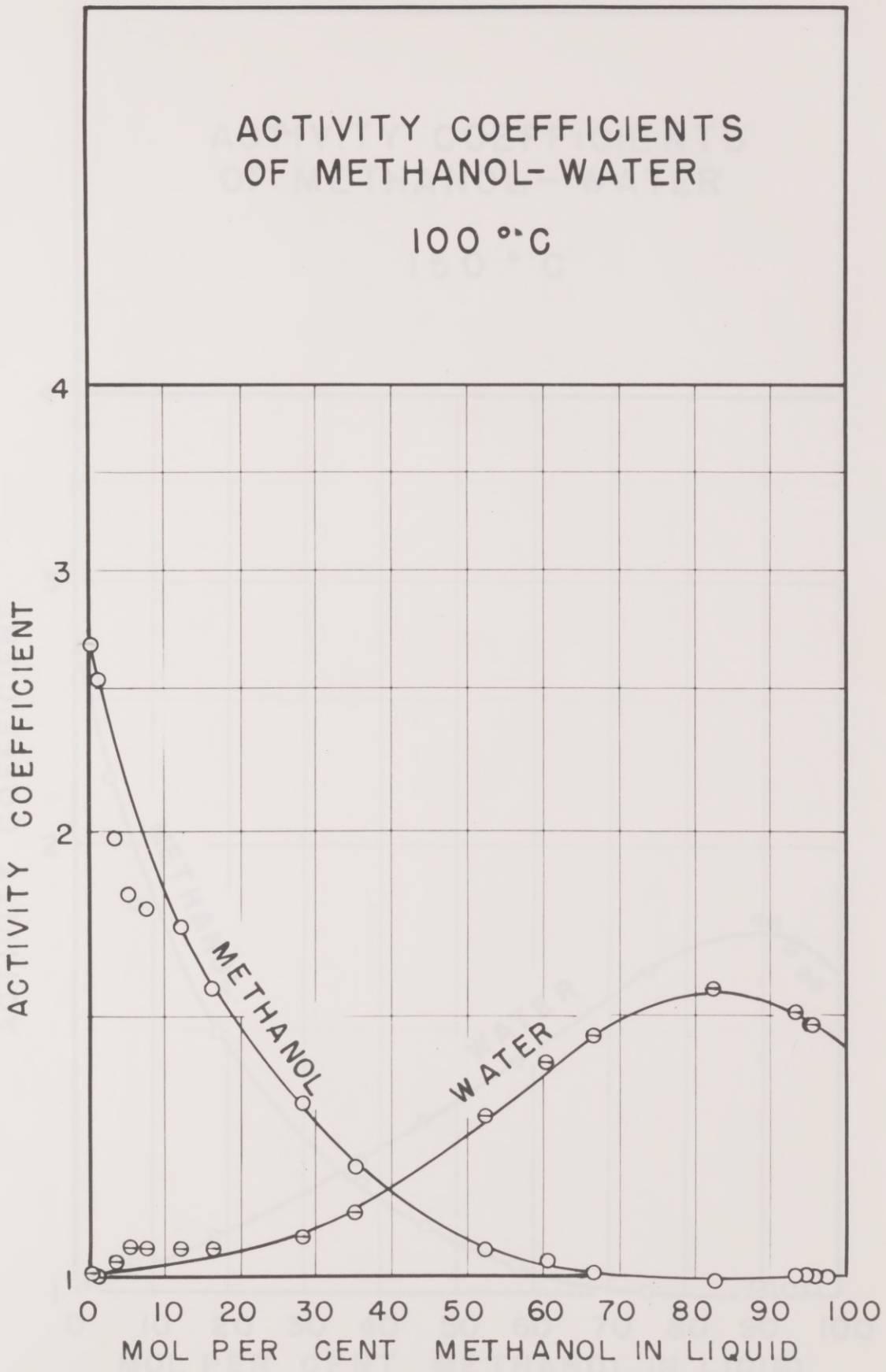

ACTIVITY COEFFICIENTS
OF METHANOL-WATER
100 °C
ACTIVITY COEFFICIENT
4
3
2
1
METHANOL
WATER
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT METHANOL IN LIQUID

FIGURE 11

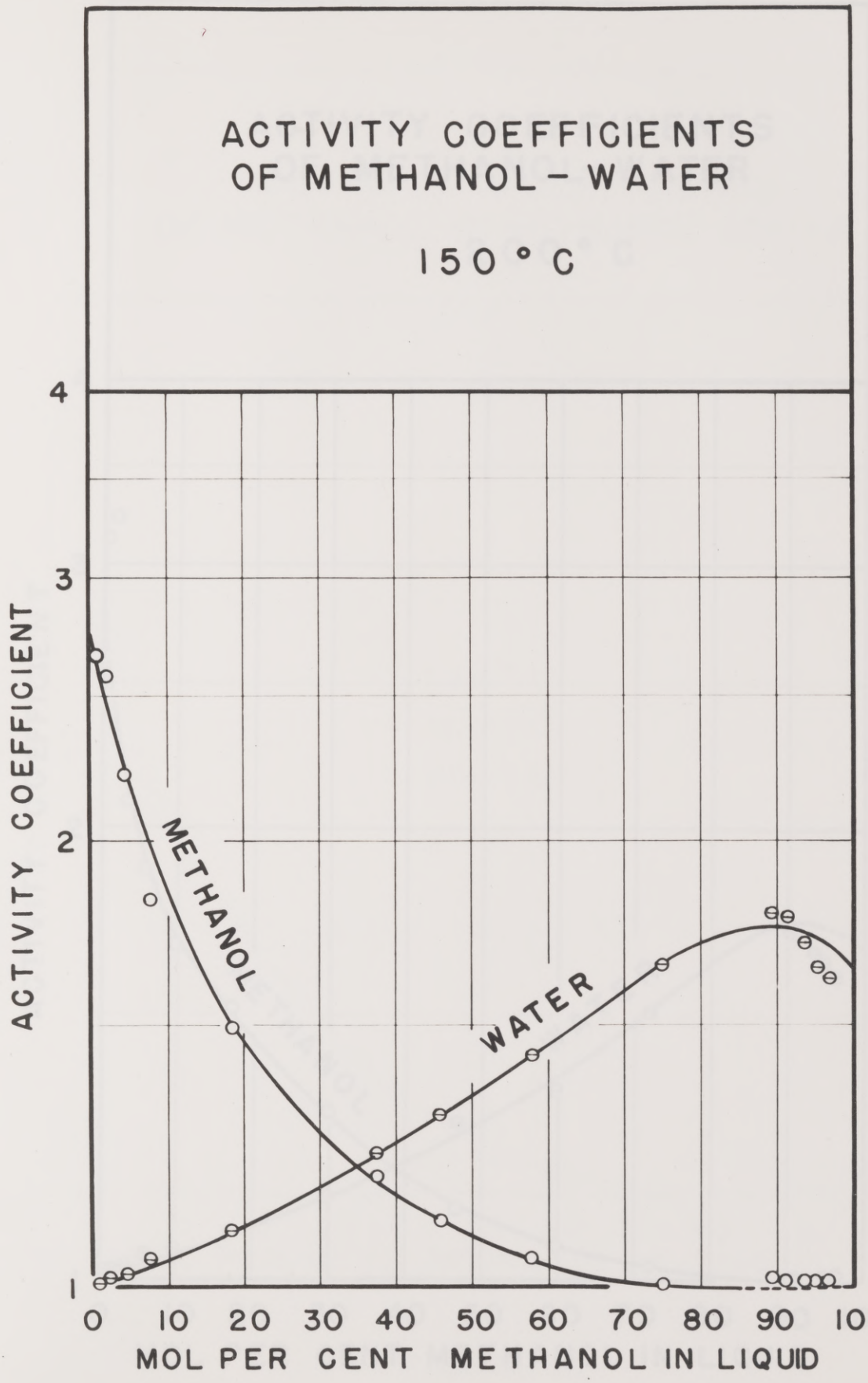

ACTIVITY COEFFICIENTS
OF METHANOL - WATER
150 ° C
ACTIVITY COEFFICIENT
4
3
2
1
METHANOL
WATER
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT METHANOL IN LIQUID

FIGURE 12

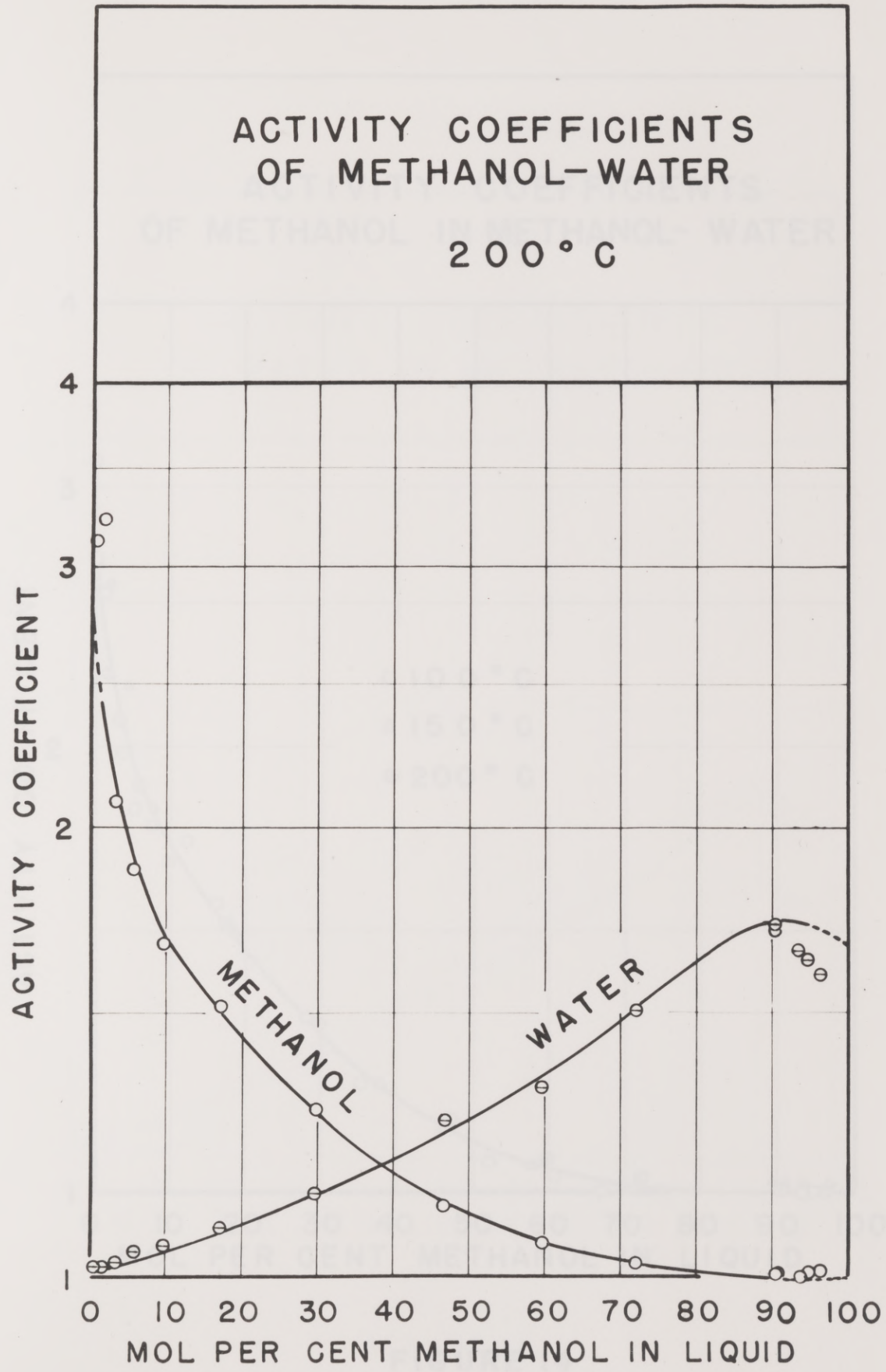

ACTIVITY COEFFICIENTS
OF METHANOL–WATER
200° C
ACTIVITY COEFFICIENT
4
3
2
1
METHANOL
WATER
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT METHANOL IN LIQUID

FIGURE 13

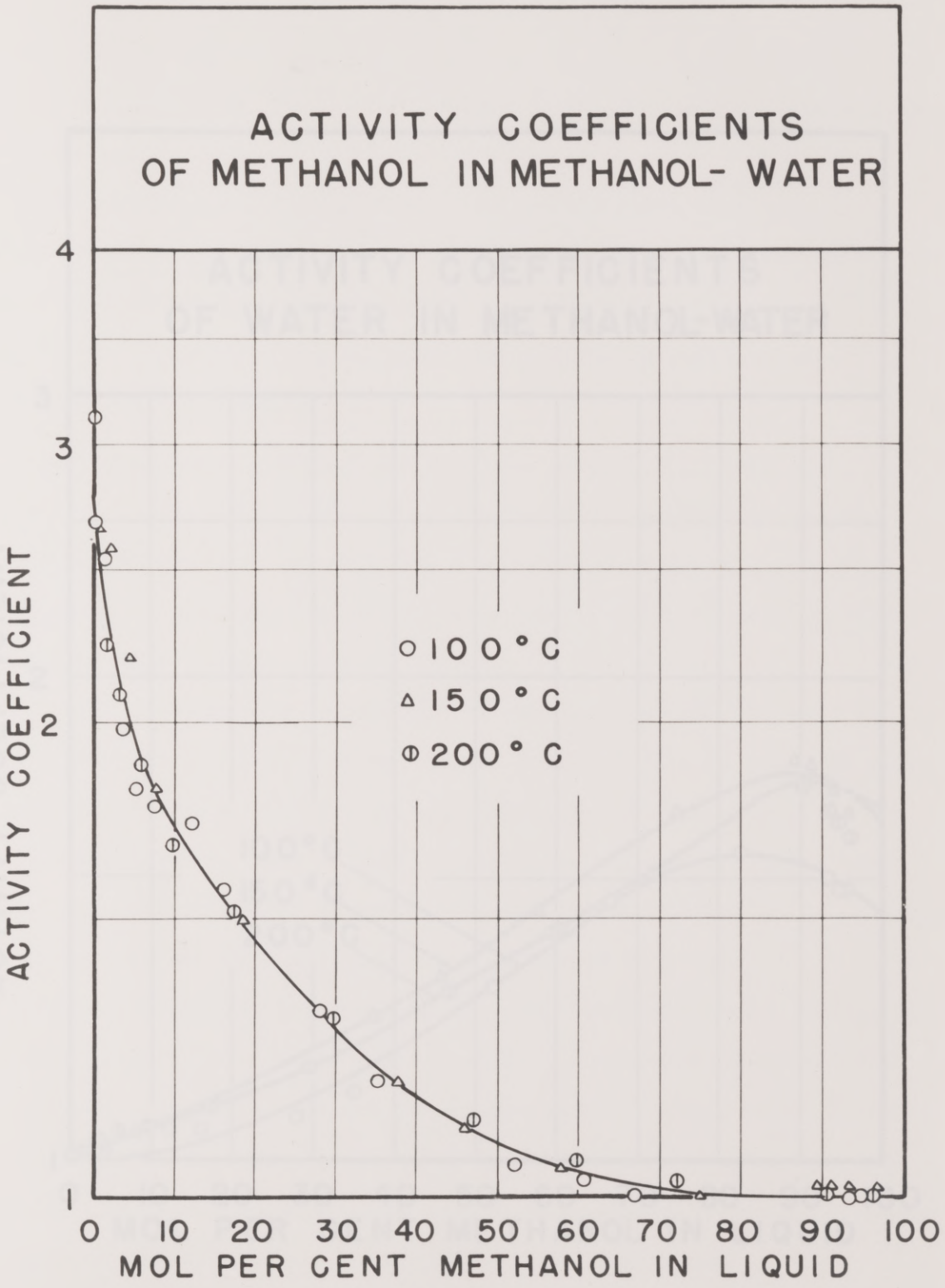

ACTIVITY COEFFICIENTS
OF METHANOL IN METHANOL- WATER
ACTIVITY COEFFICIENT
4
3
2
1
100 °C
150 °C
200 °C
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT METHANOL IN LIQUID

FIGURE 14

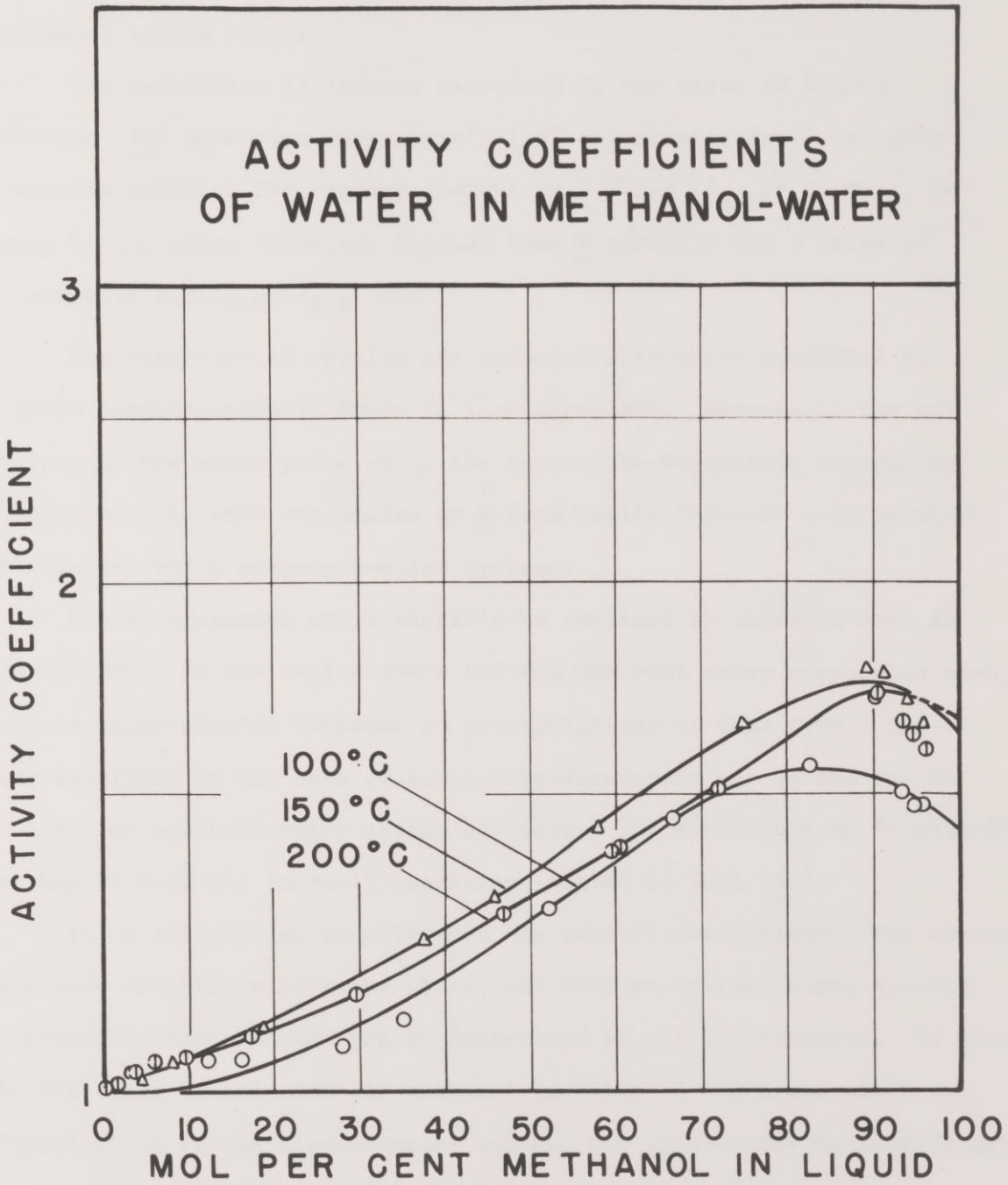

ACTIVITY COEFFICIENTS
OF WATER IN METHANOL-WATER
ACTIVITY COEFFICIENT
3
2
1
100°C
150°C
200°C
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT METHANOL IN LIQUID

FIGURE 15

where the A terms are the end constants from the activity coefficient curves as defined by Eq. (36). The subscripts 2 and 3 refer, respectively, to methanol and to water.

The expression is largely dependent on the value of D used. Rushbrooke (34) corrected Guggenheim's (16) calculation for D and gave the correct relation for regular systems as $D \geqq 2.3\ (A_{3-2})^2$. Wohl, in analogy to the above relation, assumed that D normally has a value of approximately $2.3(A_{2-3})(A_{3-2})/4$.

The experimental results are compared with those predicted by the above considerations. There is some agreement. Because of the uncertainty of the exact value of D, the Rushbrooke-Guggenheim expression was calculated to show the limits of D from Wohl's "normal" case to that of the latter which assumes regular systems.

Closer agreement could possibly be realized by improved data at 150°C and 200°C in the region where the mol per cent water approaches zero, to reduce uncertainties inherent in extrapolations of this type. The better agreement in the case of Rushbrooke-Guggenheim may be due to the fact that the methanol-water system approaches the conditions of "regularity" more than it does the "normal" conditions stated by Wohl (41).

It is interesting to note that the activity coeffieicnts for methanol change only slightly with temperature, and that an average curve closely represents the experimental points determined at all temperatures. On this basis the heats of solution for methanol in water at 100°C and above are negligible. As in the acetone-water system, the water activity coefficient curves show no simple regularity with changes in temperature.

Conditions for Inflections In Activity Coefficient Curves (Methanol-Water)

Temp., °C	γ_2' $(x_2 = 0)$	γ_3' $(x_3 = 0)$	A_{2-3}	A_{3-2}	A_{2-3}/A_{3-2}
100	2.765	1.430	0.4417	0.1553	2.85
150	2.765	1.630	0.4417	0.2122	2.08
200	2.765	1.670	0.4417	0.2227	1.98

Calculated values of A_{2-3}/A_{3-2}

Temp., °C	A_{2-3}/A_{3-2} (Wohl)	A_{2-3}/A_{3-2} (Rushbrooke)
100	2.25	2.03
150	2.25	2.04
200	2.25	2.04

where:

Wohl: $A_{2-3}/A_{3-2} > 2 + (2.3)(A_{2-3})/4$

Rushbrooke: $A_{2-3}/A_{3-2} \geqq 2 + (2.3)(A_{3-2})/12$

The isopiestic data of Othmer and Morley (33) above one atmosphere are not suitable for thermodynamic evaluation because equilibrium temperatures were not recorded. Isothermal data up to 180°C determined by Bredig and Bayer (2) are badly scattered and were not considered.

The System Acetone-Methanol

Behavior of Acetone

In the experimental work, data were first obtained for the acetone-water system, second for the methanol-water system, and then for the acetone-methanol system. Upon calculating the thermodynamic activity coefficients for the latter and plotting against liquid compositions, it was found that the results for 150°C and 200°C were discordant and not in agreement with the thermodynamic criteria of nonideal solutions. The acetone activity coefficients fell below unity as the mol fraction of acetone was increased. These curves showed little or no tendency to approach unity as the concentration of acetone approached unity. This discrepancy is more pronounced at 200°C than at 150°C.

Preliminary examination of the data on the y--x plots as they were obtained did not reveal the discrepancies. Recheck of the analytical data and instruments used eliminated their responsibility for the deviations. During the experimental runs, no unusual pressure effects were observed to indicate thermal decomposition.

It was still presumed that acetone was undergoing chemical changes which were responsible for the deviations in the results. To verify or disprove this presumption, 500 ml of purified, anhydrous acetone was charged to the equilibrium still and subjected to the standard heating period just as for an equilibrium determination. Purity of the acetone charged was certified by refractive index and density before use. After the acetone was circulated in the still for about 20 minutes at a temperature always below 100°C, a control sample was removed for checking by

refractive index and density. The control sample showed insignificant differences from the pure acetone charged.

The still was then operated at 150°C for 3 hours, after which another sample was removed. The still was then taken up to 200°C and maintained at that temperature for an hour, at the end of which time a third sample was taken. Compared to the literature vapor pressures of pure acetone, the observed pressures were about 1.5 per cent low at 150°C and about 3.4 per cent low at 200°C.

The refractive indices and densities were determined on the samples. The values were significantly higher than those of the material as charged, indicating that acetone undergoes chemical changes at temperatures above 100°C. At 150° and 200°C the increases in refractive index were equivalent to fictitious increases in acetone concentrations of 4.5 mol per cent and 14.9 mol per cent, respectively, based on the acetone-methanol refractive index analytical curve. The increases in density corresponding to the above temperatures were equivalent to fictitious increases of 1 mol per cent and 2.3 mol per cent in water, based on the acetone-water density analytical curve. These results were compared at the high acetone concentration ends of the analytical curves. The comparisons were also made with respect to the analytical data which were used for the particular systems.

The low activity coefficients obtained for acetone can be fully explained on the basis that the liquid compositions were fictitiously high in acetone. The results also indicate that the reaction is of such nature so as to produce products of higher boiling points which then remain chiefly in the liquid phase.

Several conclusions consistent with the above observations appear very plausible. It is presumed that acetone reacts to form diacetone alcohol which then splits off water to form mesityl oxide according to the reaction

$$2\ CH_3COCH_3 \longrightarrow (CH_3)_2COHCH_2COCH_3$$

$$\longrightarrow (CH_3)_2C{=}CHCOCH_3 \quad + \quad H_2O$$

The reaction occurs readily in the presence of certain catalysts (7). It is not known as to what extent it may occur at the temperatures and conditions in question.

The refractive indices and densities of diacetone alcohol and mesityl oxide are higher than those of acetone. Water has a lower refractive index than acetone, but it causes increases in refractive index of mixtures with acetone up to a certain concentration (15).

Experimental and Calculated Data

Although the vapor-liquid equilibrium data have been determined experimentally at 100°C, 150°C, and 200°C, only those at 100°C are reliable at high acetone concentrations. The data are given in Tables IX, X, and XI and are plotted in Figure 16. Activity coefficient-composition curves are given in Figure 17 for 100°C. Those calculated at 150°C and 200°C are included in the tables but were not plotted.

The problem immediately presented itself as to what could be done to examine and correct the data such the probable error or

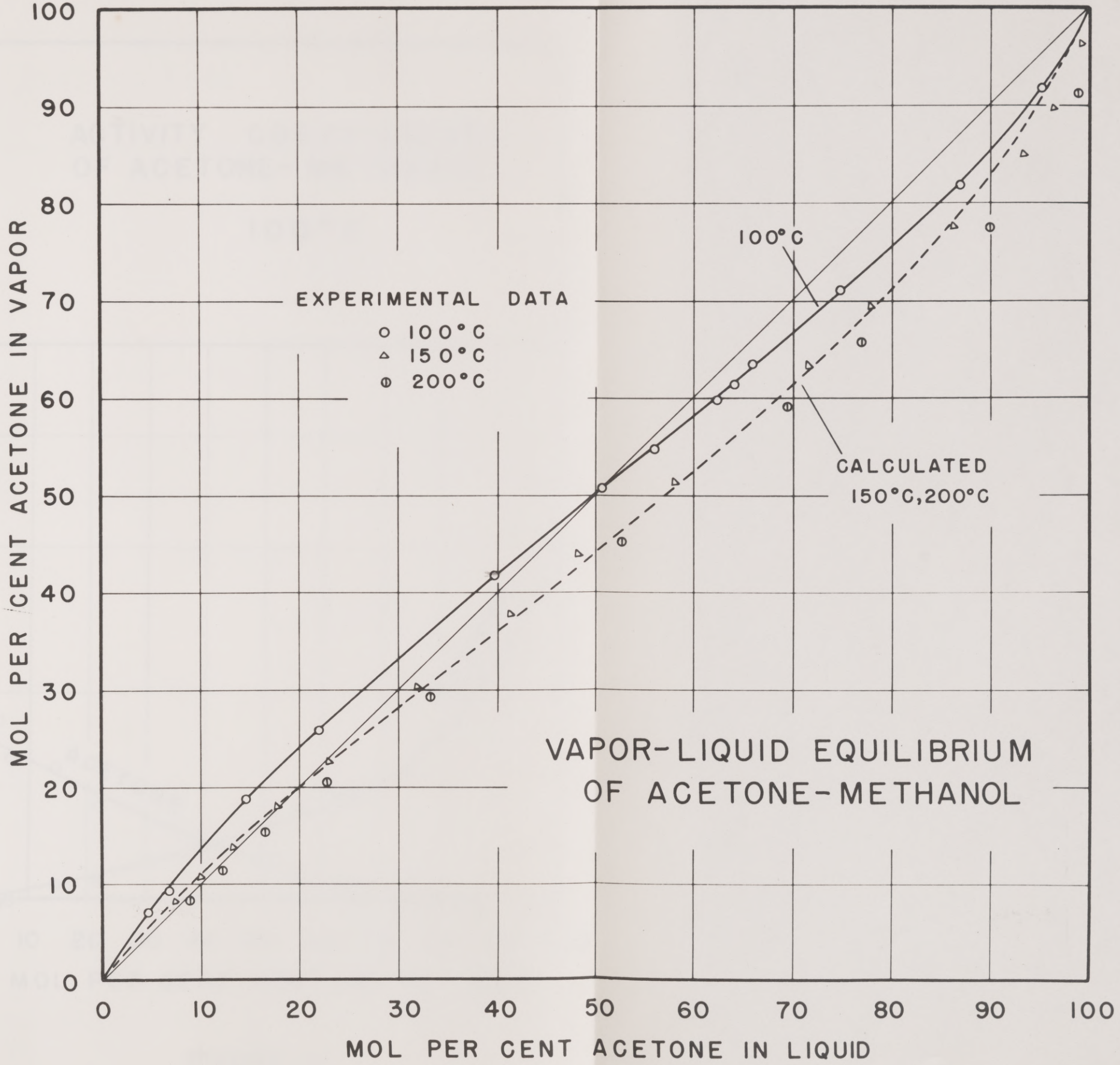

EXPERIMENTAL DATA
○ 100°C
△ 150°C
⊖ 200°C
100°C
CALCULATED
150°C,200°C
VAPOR-LIQUID EQUILIBRIUM
OF ACETONE-METHANOL
MOL PER CENT ACETONE IN VAPOR
MOL PER CENT ACETONE IN LIQUID
0
10
20
30
40
50
60
70
80
90
100

FIGURE 16

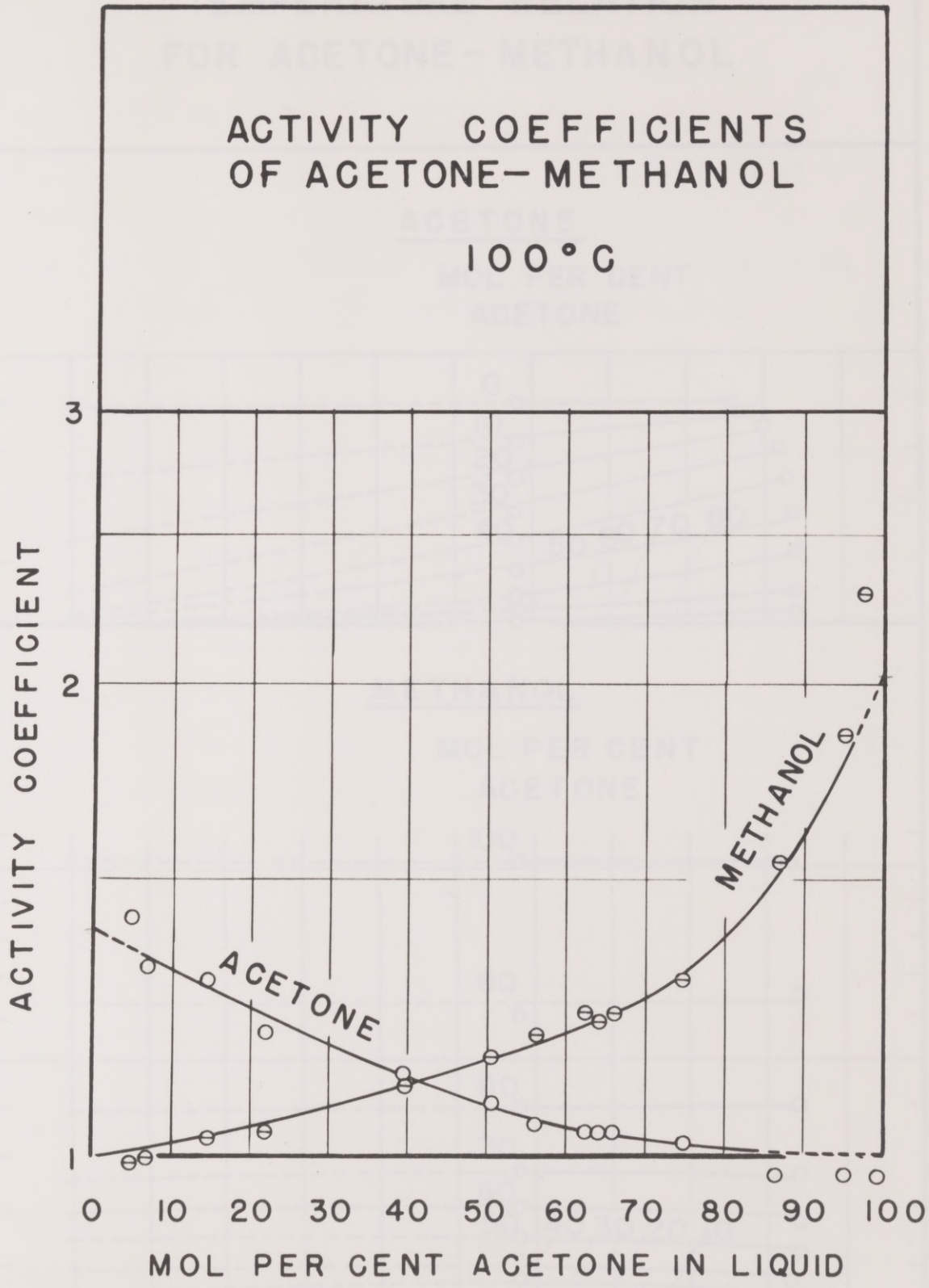

ACTIVITY COEFFICIENTS
OF ACETONE–METHANOL
100°C
ACTIVITY COEFFICIENT
3
2
1
ACETONE
METHANOL
0 10 20 30 40 50 60 70 80 90 100
MOL PER CENT ACETONE IN LIQUID

FIGURE 17

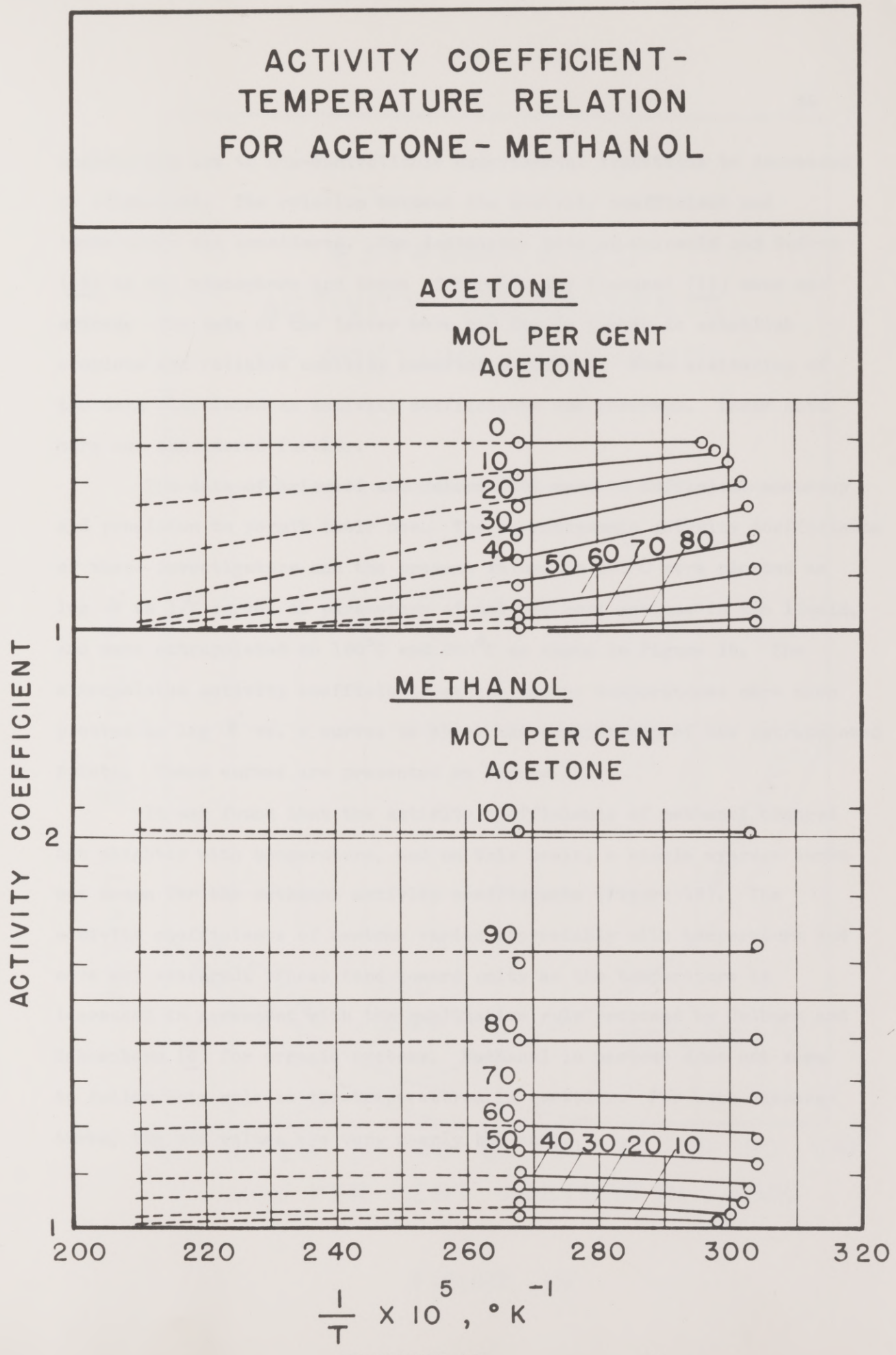

ACTIVITY COEFFICIENT-
TEMPERATURE RELATION
FOR ACETONE-METHANOL
ACETONE
MOL PER CENT
ACETONE
0
10
20
30
40
50 60 70 80
METHANOL
MOL PER CENT
ACETONE
100
90
80
70
60
50 40 30 20 10
ACTIVITY COEFFICIENT
1
2
1
200
220
240
260
280
300
320
1/T X 10^5, °K^-1

FIGURE 18

uncertainty due to non-controllable experimental conditions be decreased or eliminated. The relation between the activity coefficient and temperature was considered. The isopiestic data of Griswold and Buford (15) at one atmosphere and those of Fordyce and Simonsen (12) were examined. The data of the latter were too few in number to establish complete and reliable activity coeeficient curves. Some scattering of the data claculated as activity coefficients was observed. These data were not considered further.

The data of Griswold and Buford (15) were of sufficient accuracy and precision to permit their use. The thermodynamic activity coefficients of these investigators and the present values at 100°C were plotted as log γ' vs 1/T curves at parameters of mol per cent acetone in the liquid, and were extrapolated to 150°C and 200°C as shown in Figure 18. The extrapolated activity coefficients at the latter temperatures were then plotted as log γ' vs. x curves to check the consistency of the extrapolated points. These curves are presented on Figure 19.

It was found that the activity coefficients of methanol changed but slightly with temperature, and on this basis, a single average curve was drawn for the methanol activity coefficients (Figure 19). The activity coefficients of acetone varied appreciably with temperature and were not averaged. These tend toward unity as the temperature is increased in agreement with the qualitative rule proposed by Colburn and Schoenborn (6) for organic systems. Methanol in acetone does not seem to follow this rule at the temperatures in question. For both temperatures, the end values are very nearly the same.

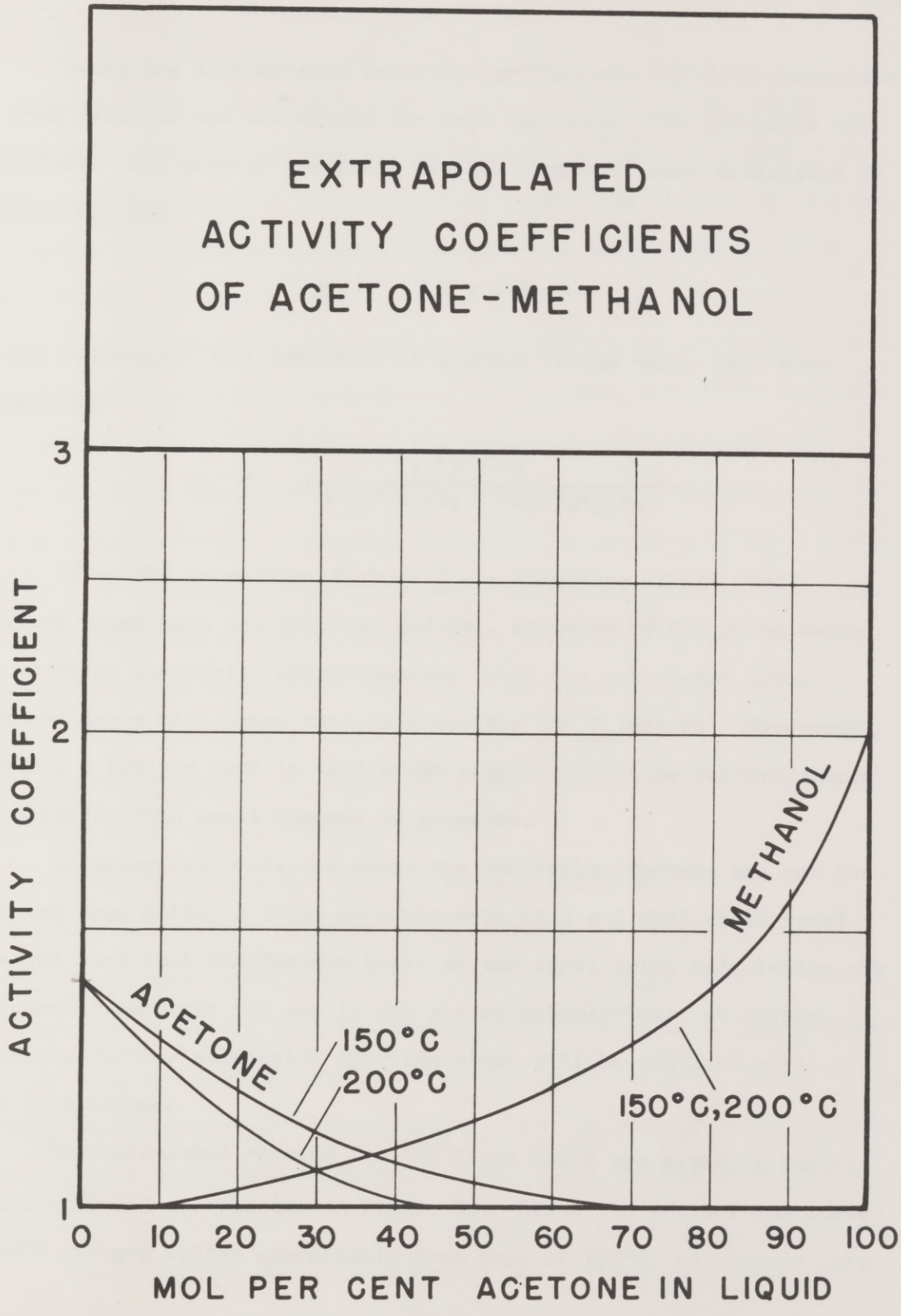

EXTRAPOLATED
ACTIVITY COEFFICIENTS
OF ACETONE-METHANOL
ACTIVITY COEFFICIENT
3
2
1
0
10
20
30
40
50
60
70
80
90
100
MOL PER CENT ACETONE IN LIQUID
METHANOL
ACETONE
150°C
200°C
150°C,200°C

FIGURE 19

Using the extrapolated activity coefficients for both components, the y--x relation was calculated for each isotherm. The procedure was as follows: The partial pressures of each component were calculated by applying Eq. (5)

$$\pi y = \gamma' P x / Z$$

to each component. Mol fractions of acetone in the vapor were then computed by

$$y_1 = \frac{\gamma'_1 P_1 x_1 / Z_1}{\gamma'_1 P_1 x_1 / Z_1 + \gamma'_2 P_2 x_2 / Z_2}$$

Since the correction factors Z are functions of the total pressures which have not yet been decided, solution of the above equation requires successive approximations until the calculated total pressures agree with those used in obtaining the Z factors. Agreement to within a few per cent is sufficient as the correction factors change very slightly with small changes in pressure.

At moderated pressures where the correction factors are not too different from unity, a first approximation of Z = 1 will yield total pressures such that the factors based on the first trial calculation are sufficiently accurate for use in the second calculation. At higher pressures, further successive approximations will be required until a match is obtained.

The calculated results for 150°C and 200°C are given in Tables XII and XIII and are plotted in Figure 16. Since the equilibrium curve at 200°C did not differ appreciably from that at 150°C, an average curve

was drawn to represent the y--x data for both temperatures. There is essentially coincidence of the curves up to 20 mol per cent acetone in liquid, and also above 90 mol per cent acetone. The maximum difference between the curves is only a little more than 1 mol per cent acetone in the vapor.

These results are not inconsistent with the principles of vapor-liquid equilibria. As the temperature is increased from 100°C to 150°C the equilibrium curve is displaced away from the 45° reference line because the vapor pressure of methanol crosses that of acetone, and it becomes the more-volatile component at temperatures above 115°C. Further increases in temperature require that the equilibrium curves move back toward the 45° line as the relative volatilities are reduced and liquid-vapor compositions tend toward equality. Of course, at and above the critical, vapor and liquid compositions become identical or fall on the 45° line. The practical coincidence of the 150° and 200°C isotherms is a consequence of the two opposing factors.

It is to be expected that in low concentrations, there would be little or no chemical changes of the acetone, and that the calculated data should agree with the experimental data at 150°C if the extrapolation is reliable. From Figure 16 it is seen that the agreement is quite good up to 25 mol per cent acetone in the liquid. The largest differences would be expected in the high acetone concentrations where chemical change should be most rapid. This was also found to be true as seen in Figure 16.

The calculated total pressures at 150°C agree with those observed. While the experimental total pressure data are not extremely

accurate, they should be approximately correct. The greatest difference between calculated and experimental total pressures is 3 per cent, with the calculated values being higher at acetone concentrations above 80 mol per cent. Below 30 mol per cent acetone, the calculated values are about 1 per cent lower. Between these concentrations, calculated total pressures are about 1 to 2 per cent higher. The changes in the acetone at 150°C cause a vapor pressure depression of approximately 1.5 per cent.

Total pressures calculated for 200°C do not agree well with the experimental values. The fictitious analytical values due to changes at this temperature make such a comparison unreliable. Maximum differences are 10 per cent higher for the calculated values, and thelatter are believed to be very nearly the true figures.

Azeotropism

The following minimum-boiling azeotropes were found for acetone-methanol at the temperatures noted:

100°C	50.7 mol per cent acetone
150°C	21.9 mol per cent acetone
200°C	19.2 mol per cent acetone
150°C, 200°C	20.6 mol per cent acetone (from average curve, Figure 16)

At 115°C the vapor pressures of acetone and methanol are equal, and above that temperature, the vapor pressure of methanol is greater than that of acetone. This accounts for the decreasing acetone concentrations in the azeotropes at temperatures above 100°C.

Britton, Nutting, and Horsley (3) have published their results for the acetone-methanol system at elevated pressures. The data are rather sketchy and no details are given of the experimental procedures used. It was stated that acetone and methanol do not form azeotropes above 290 psia. No mention was made regarding the chemical changes in acetone at elevated temperatures. The method of analysis was not disclosed.

The System Acetone-Methanol-Water

Experimental The vapor-liquid equilibrium data for this system have been determined at 100°C and 250°C. The data are given in Table XIV and in Table XV, respectively. The ternary diagram at 100°C is given in Figure 20. The isoforms at 100° are similar in shape to those determined by Griswold and Buford (15) for this system at 760 mm Hg. The vapor isoforms tend to converge as the concentration of water increases. A separate and enlarged plot, Figure 21, of the high-water concentration portion of the ternary diagram was prepared to permit greater ease in reading. Equilibrium pressures as a function of the liquid composition are given in Figure 22.

The y--x data for the system at 250°C are plotted in Figure 23. The vapor isoforms have the same general shapes as those at lower temperatures except near the critical locus. As the mol per cent methanol increases, the isoforms deviate from their usual shapes and finally converge to the critical of methanol-water. As to be expected, the curvatures of the isoforms at 250°C are much less than at 100°C.

The critical locus of mixtures with a critical temperature of 250°C was established as follows: A sufficient number of experimental points were run to determine accurately the shapes of the isoforms of mol per cent acetone in the vapor. Towards the high methanol end of the diagram, the water isoforms were carefully established. At the critical, vapor and liquid phases merge and compositions are identical. The intersection of the acetone and water vapor isoforms at their respective

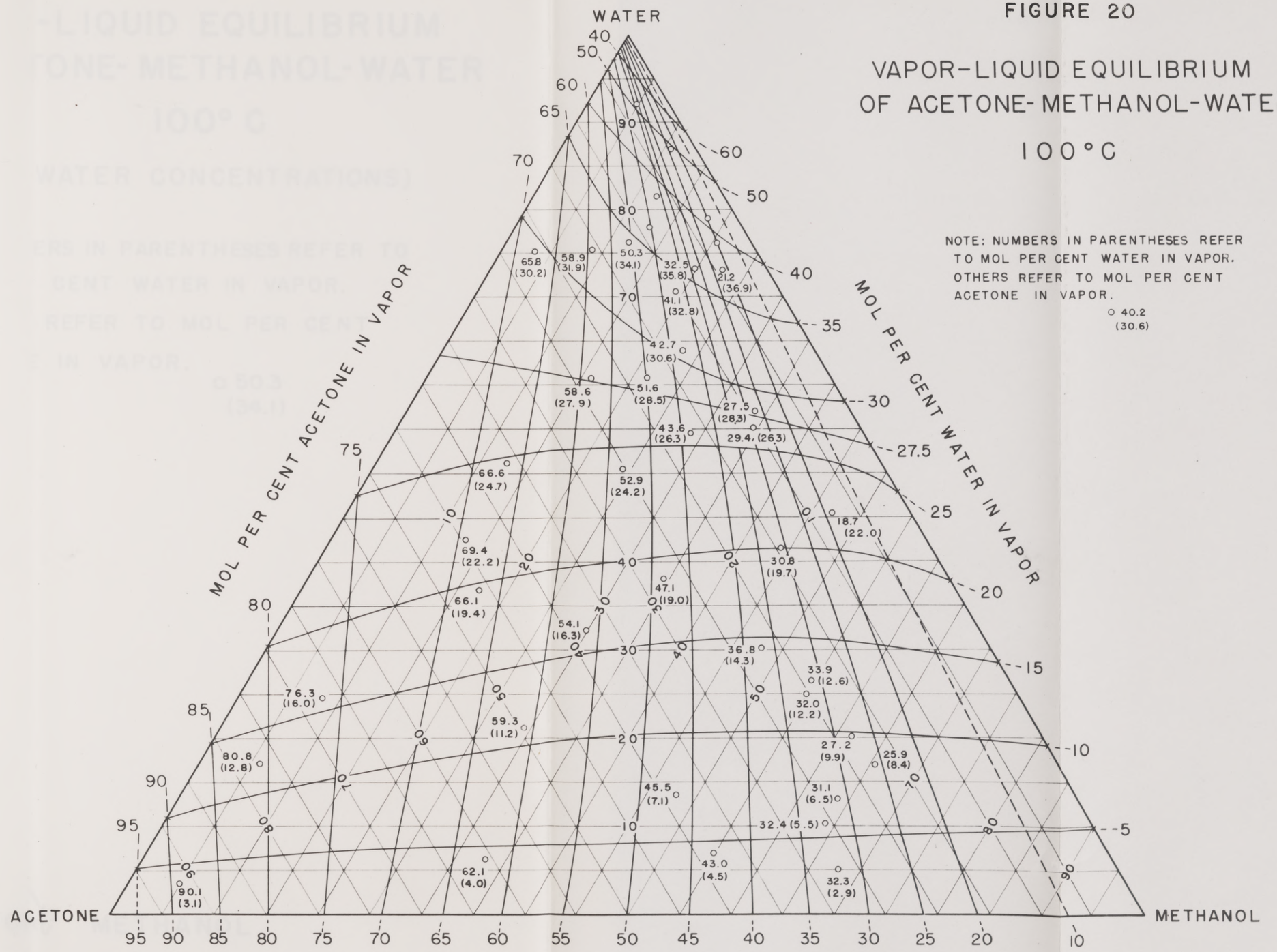


FIGURE 20

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

100°C

NOTE: NUMBERS IN PARENTHESES REFER TO MOL PER CENT WATER IN VAPOR. OTHERS REFER TO MOL PER CENT ACETONE IN VAPOR.

○ 40.2
(30.6)

FIGURE 21

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER 100° C

(HIGH WATER CONCENTRATIONS)

NOTE: NUMBERS IN PARENTHESES REFER TO MOL PER CENT WATER IN VAPOR. OTHERS REFER TO MOL PER CENT ACETONE IN VAPOR.

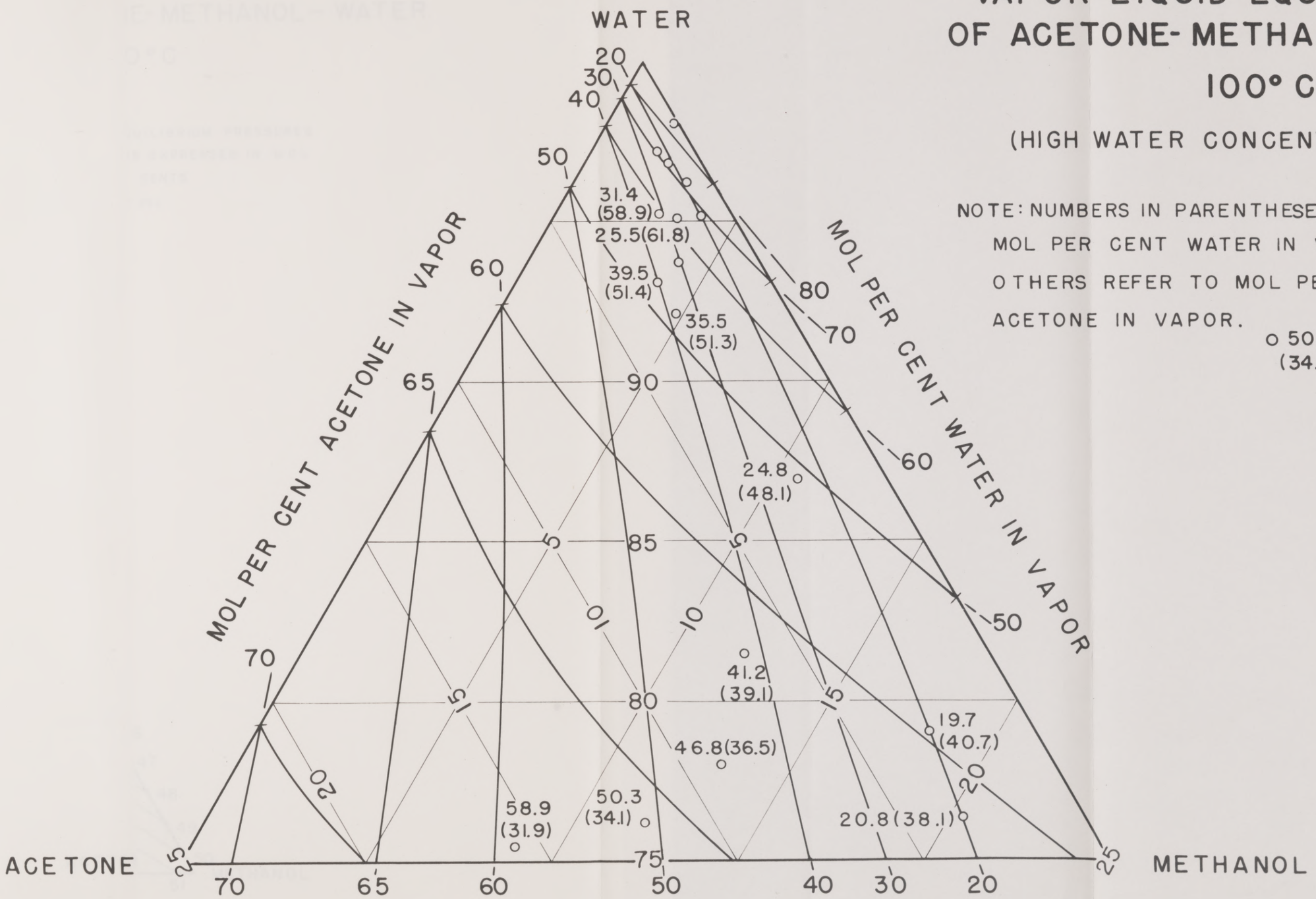
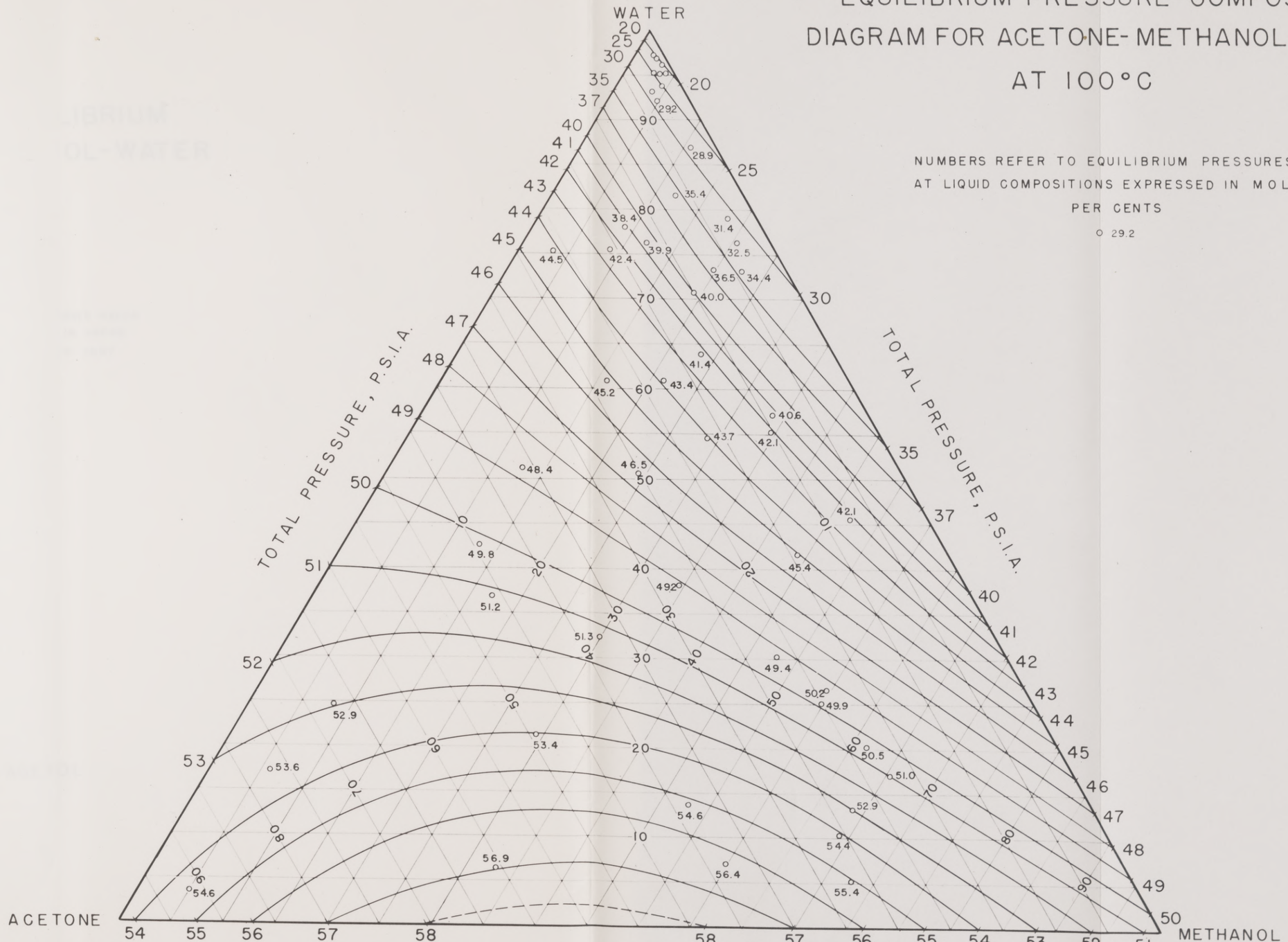


FIGURE 22

EQUILIBRIUM PRESSURE-COMPOSITION DIAGRAM FOR ACETONE-METHANOL-WATER AT 100°C

NUMBERS REFER TO EQUILIBRIUM PRESSURES AT LIQUID COMPOSITIONS EXPRESSED IN MOL PER CENTS

○ 29.2



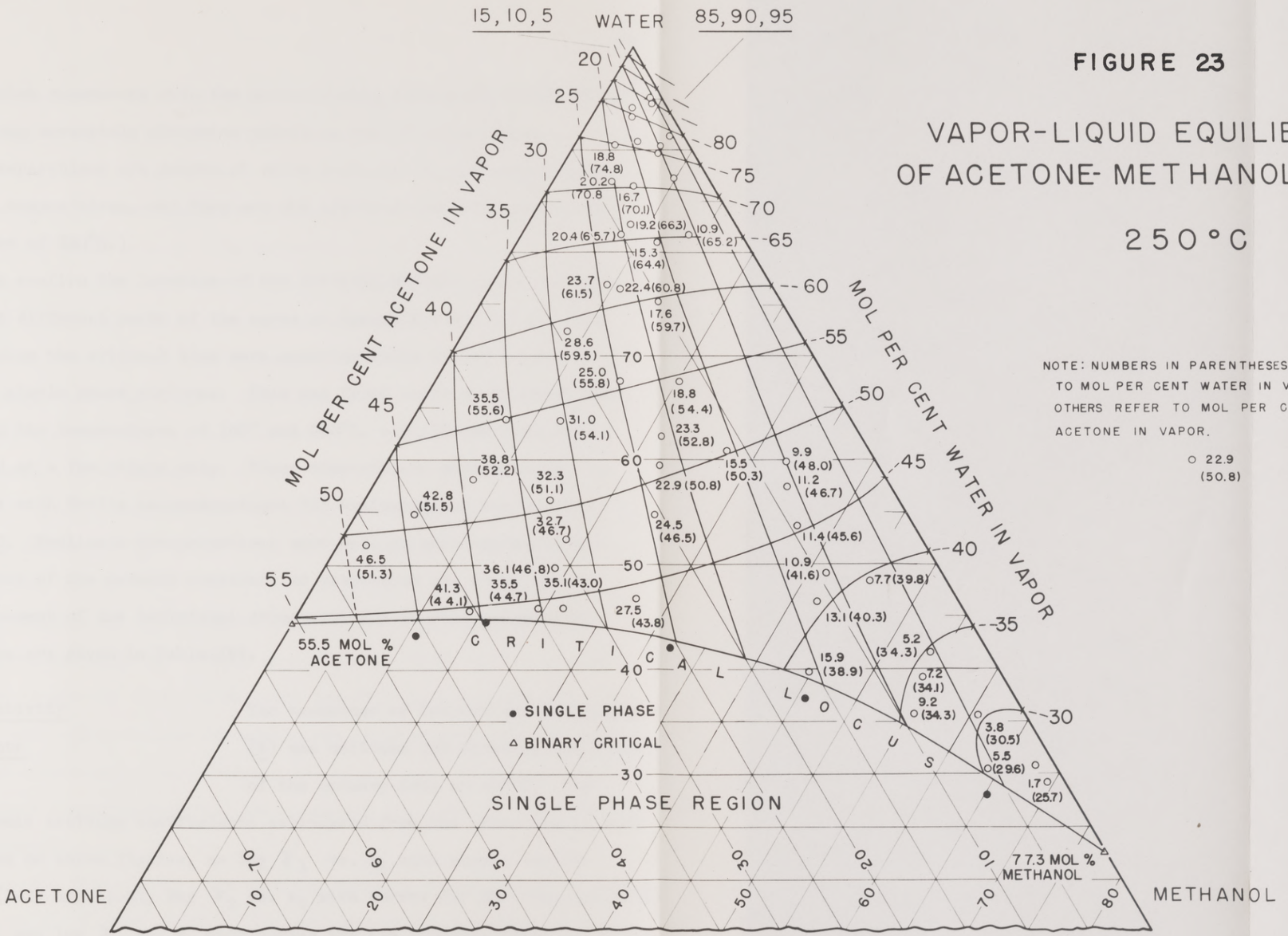


FIGURE 23

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

250°C

NOTE: NUMBERS IN PARENTHESES REFER TO MOL PER CENT WATER IN VAPOR. OTHERS REFER TO MOL PER CENT ACETONE IN VAPOR.

○ 22.9
(50.8)

concentration parameters with the corresponding curves for liquid phase compositions accurately determine points on the critical locus. (These intersections are points at which vapor and liquid phases reach identical compositions, and they are the critical compositions for the temperature of 250°C.)

To confirm the location of the critical mixture curve, numerous samples at different parts of the curve at compositions slightly lower in water than the critical line were experimentally tested to see if they were single phase mixtures. This was found to be so in every case.

At the temperatures of 150° and 200°C, equilibrium data were determined at a few points only. These compositions were selected in accordance with Wohl's recommendations for evaluation of the ternary constant C. Duplicate determinations were made at each temperature. The accuracy of the ternary constants so determined are shown by the close agreement of the individual determinations at each temperature. The results are given in Table XVI.

Ternary Activity Coefficients

The technique of Colburn and Schoenborn (6) was utilized for plotting and study of the ternary data at 100°C. The thermodynamic activity coefficients calculated from the experimental data are plotted on three figures, as log γ'_1 vs. x_1 with curves for the binaries (1-2) and (1-3), log γ'_2 vs. x_2 with curves for the binaries (2-1) and (2-3), and log γ'_3 vs. x_3 with curves for the binaries (3-1) and (3-2). In this work, 1, 2, and 3 refer to acetone, methanol, and water, respectively.

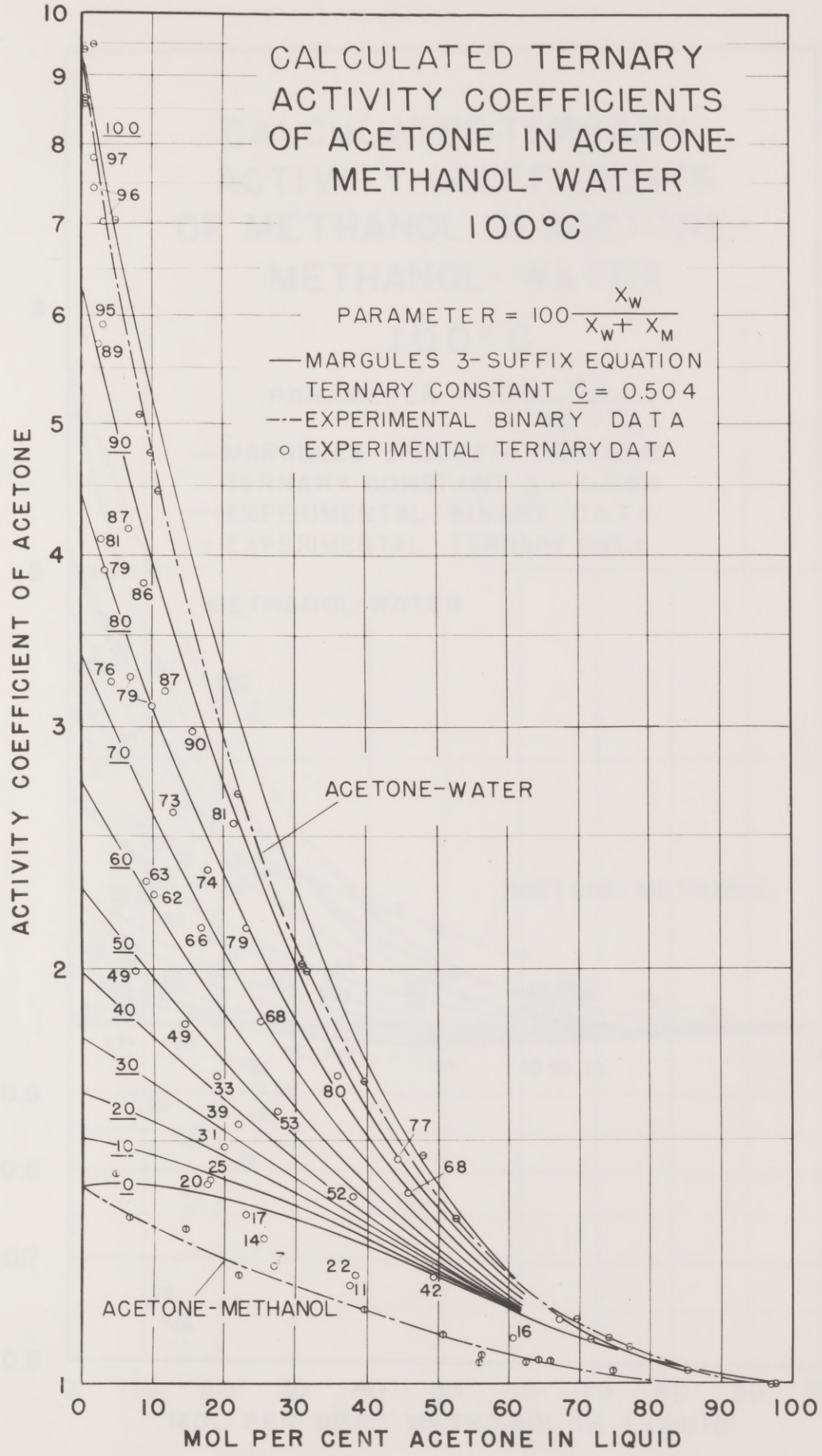

CALCULATED TERNARY ACTIVITY COEFFICIENTS OF ACETONE IN ACETONE-METHANOL-WATER 100°C
PARAMETER = 100 $\frac{X_W}{X_W + X_M}$
—MARGULES 3-SUFFIX EQUATION
TERNARY CONSTANT C = 0.504
---EXPERIMENTAL BINARY DATA
○ EXPERIMENTAL TERNARY DATA
ACETONE-WATER
ACETONE-METHANOL
ACTIVITY COEFFICIENT OF ACETONE
MOL PER CENT ACETONE IN LIQUID
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100

FIGURE 24

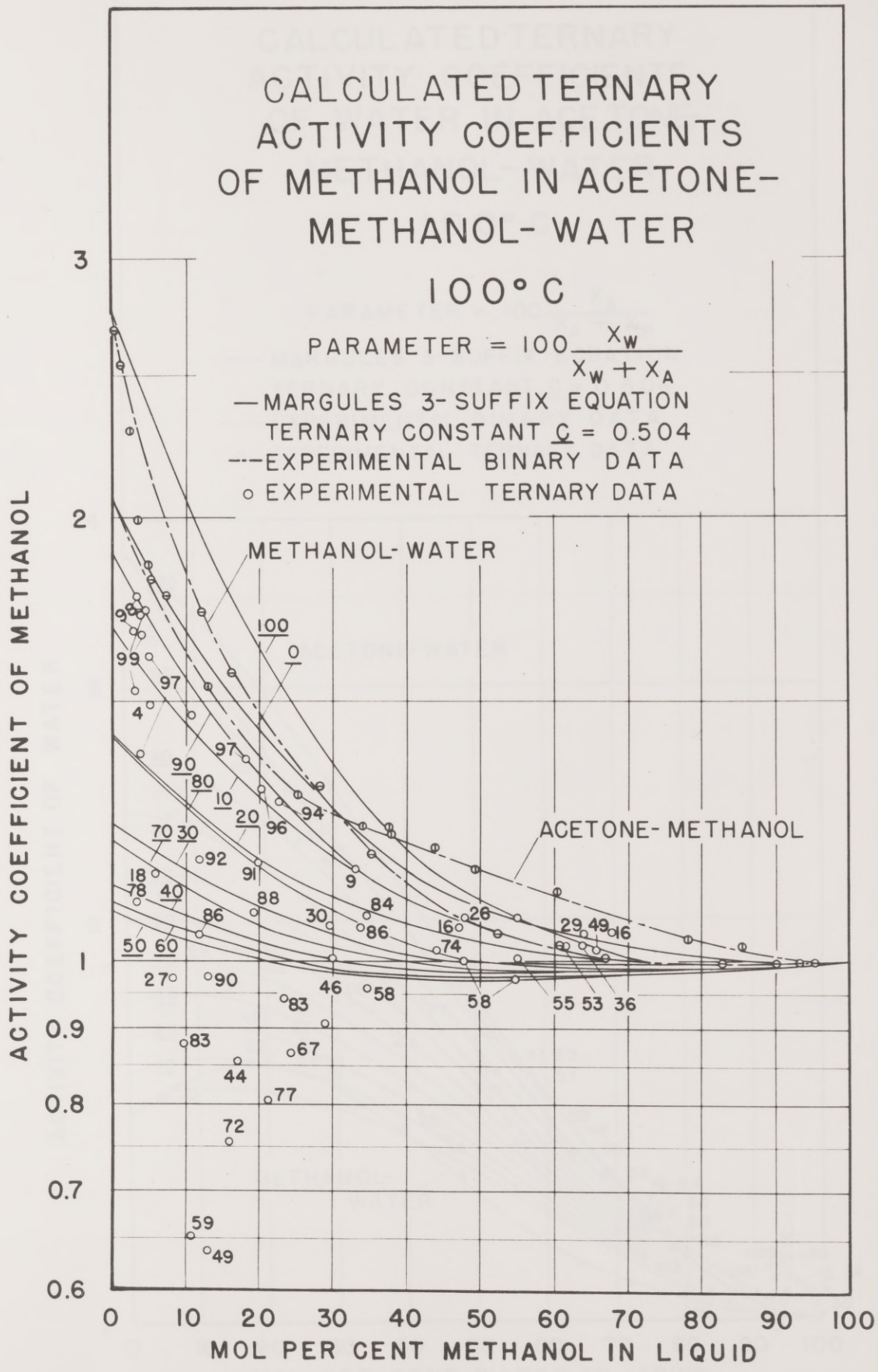

CALCULATED TERNARY
ACTIVITY COEFFICIENTS
OF METHANOL IN ACETONE-
METHANOL- WATER
100° C
PARAMETER = 100 $\frac{X_W}{X_W + X_A}$
—MARGULES 3-SUFFIX EQUATION
TERNARY CONSTANT C = 0.504
---EXPERIMENTAL BINARY DATA
o EXPERIMENTAL TERNARY DATA
METHANOL-WATER
ACETONE-METHANOL
ACTIVITY COEFFICIENT OF METHANOL
MOL PER CENT METHANOL IN LIQUID
3
2
1
0.9
0.8
0.7
0.6
0
10
20
30
40
50
60
70
80
90
100

FIGURE 25

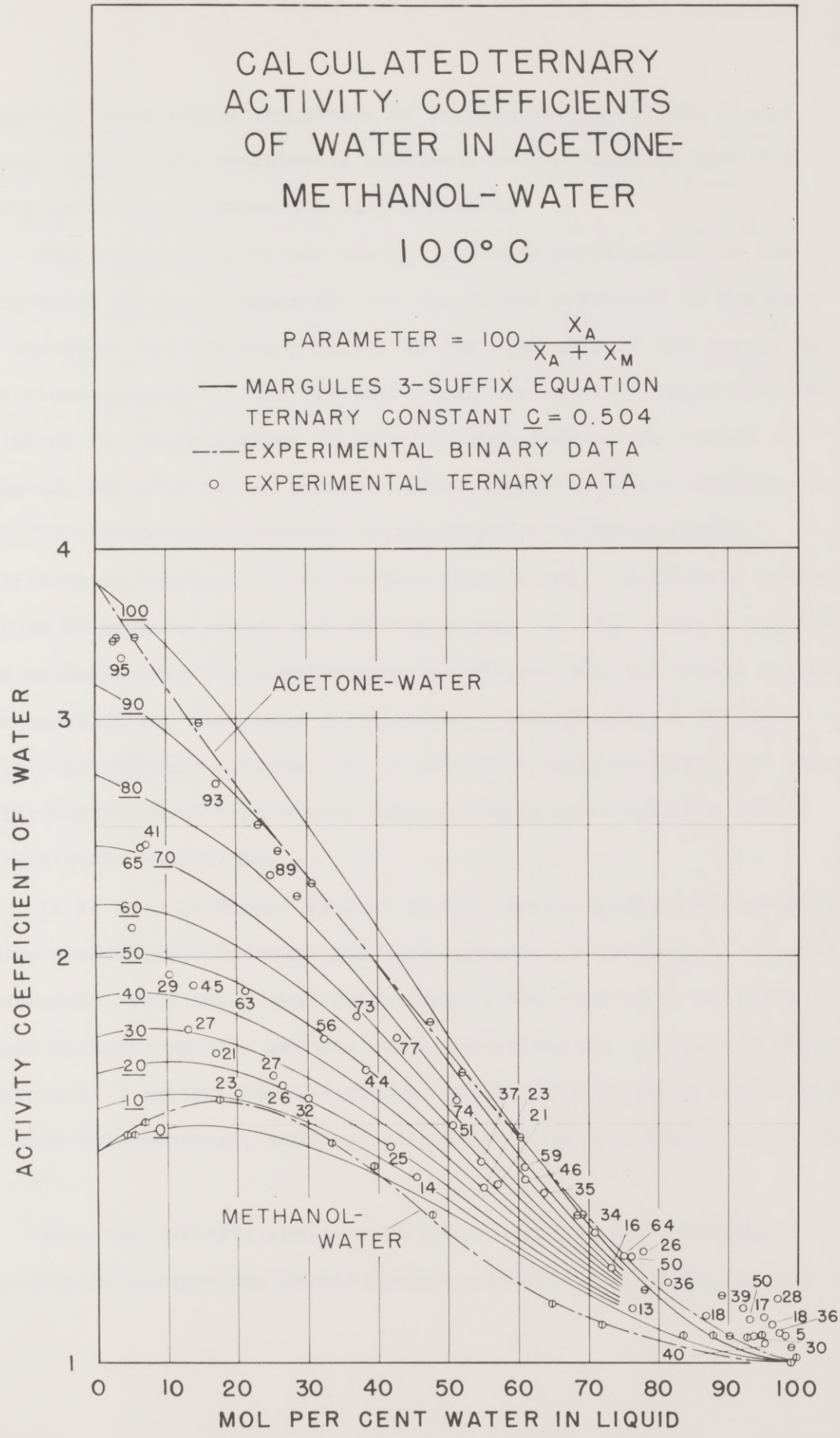

CALCULATED TERNARY ACTIVITY COEFFICIENTS OF WATER IN ACETONE-METHANOL-WATER 100° C
PARAMETER = 100 X_A / (X_A + X_M)
MARGULES 3-SUFFIX EQUATION
TERNARY CONSTANT C = 0.504
EXPERIMENTAL BINARY DATA
EXPERIMENTAL TERNARY DATA
ACTIVITY COEFFICIENT OF WATER
MOL PER CENT WATER IN LIQUID
ACETONE-WATER
METHANOL-WATER
0
10
20
30
40
50
60
70
80
90
100
1
2
3
4

FIGURE 26

be expected from Wohl's exposition of characteristics of the binary equations (41). Only qualitative agreement may be expected when the activity coefficient curves are unsymmetrical.

Fair correlation of the acetone activity coefficients in the acetone-water system is obtained, but the curves predicted by the Margules equations are not steep enough at the high ends of the curves to permit close agreement. The van Laar equations should provide a better correlation for these systems if only the high ends of the curves are considered, but they cannot provide curves having maxima or minima.

Of considerable interest is the behavior of the activity coefficients of methanol in the ternary (Figure 23). The binary curves are those of methanol-water and acetone-water. In this case, a majority of the methanol activity coefficients lie without the two binary curves. This connection was also observed by Colburn and Schoenborn (6) in certain other ternary systems. It is now known that prediction of ternary activity coefficients from binary data by simple interpolation is unsound and quite unreliable.

It is seen in Figure 25 that in the ternary mixture the methanol activity coefficients decrease and then increase as the amount of water is increased. This means that water reduces the volatility of methanol in these mixtures up to a certain water concentration, and beyond which it increases it again. The calculated activity coefficients qualitatively agree with this behavior, although the correlation as a whole is not too good.

From the activity coefficient plots, despite the divergencies between the calculated and experimental activity coefficients for the

binaries, the data indicate that the ternary equations will correlate correctly and with reliability within certain composition ranges. A great number of determinations of high precision would be required to ascertain the range of applicability of the equations from such plots alone. Since complete equilibrium data have been determined at 100°C, direct evaluation of the equations can be made by comparison of calculated equilibrium data to the experimental results.

Ternary Calculations

As previously discussed, application of the Margules ternary equations requires six binary constants and the ternary constant C. The ternary constant may be evaluated from a single ternary point by solution of one of the ternary equations after the binary constants have been determined. The ternary constant term's contribution to the activity coefficient is often considerable, and for this reason C must be known to considerable accuracy, or determined from more than one experimental point. For the 100°C calculations two points were chosen, each with approximately equal concentrations of two components with the remaining one at some low concentration. The low concentration component in one case was acetone while in the second case it was water. The values of C so obtained were 0.502 and 0.506 respectively. The average of 0.504 was used. The very close agreement indicates the general accuracy of the experimental data. The results of these calculations are summarized in Table XVI.

The procedure was as follows: The experimentally determined binary data fix the ends of the vapor isoforms. To fix the general shapes

of these curves at their approximate midpoints, arbitrary liquid compositions were taken along the line of equal mol fractions of acetone and methanol. Along this parameter, the exact ternary liquid compositions were then taken at increments of 5 mol per cent water. The closeness of water concentration increments was chosen to reduce the amount of interpolation necessary to obtain the isoforms at integral values of water concentrations. The calculations were extended well into the high water concentration range to observe the equations' applicability.

Thermodynamic activity coefficients were calculated for each component at the arbitrary liquid compositions. To obtain the corresponding y--x data, Eq. (5) containing the Z correction factor must be used. The partial pressures of each component were calculated and then added to obtain the total pressure. The ratio of the partial to the total pressure gave the mol fraction of the specified component in the vapor. The general equation may be written,

$$y_1 = \frac{\dfrac{\gamma'_1 P_1 x_1}{Z_1}}{\dfrac{\gamma'_1 P_1 x_1}{Z_1} + \dfrac{\gamma'_2 P_2 x_2}{Z_2} + \dfrac{\gamma'_3 P_3 x_3}{Z_3}} \qquad (42)$$

It is to be remembered that Z is a function of the total pressure and correct solution to Eq. (42) requires successive approximations to obtain correspondence between the pressures at which the Z's were obtained and the final total pressures. The procedure is similar to that described for the calculations on the acetone-methanol binary.

For the 100°C isotherm the first approximation gave total pressures of sufficient accuracy to obtain reliable values of the correction factors. To establish the shape of the isoform predicted by the ternary equations, calculations were made to determine this in the moderately high water concentration portion of the diagram. A summary of the calculated data is given in Table XX. The calculated and experimental data are compared in Figure 27. From this plot, it is seen that the Margules equations will predict the shapes of the water isoforms satisfactorily up to about 30 mol per cent water in the liquid. As the concentration of water increases further, deviations between calculated and experimental values become greater. The actual curvature is reduced and then reversed with increasing water concentrations, whereas the correlation predicts continually increasing curvature. These deviations lie in the direction of too low water concentrations in the vapor.

Calculated and Predicted Ternary Data

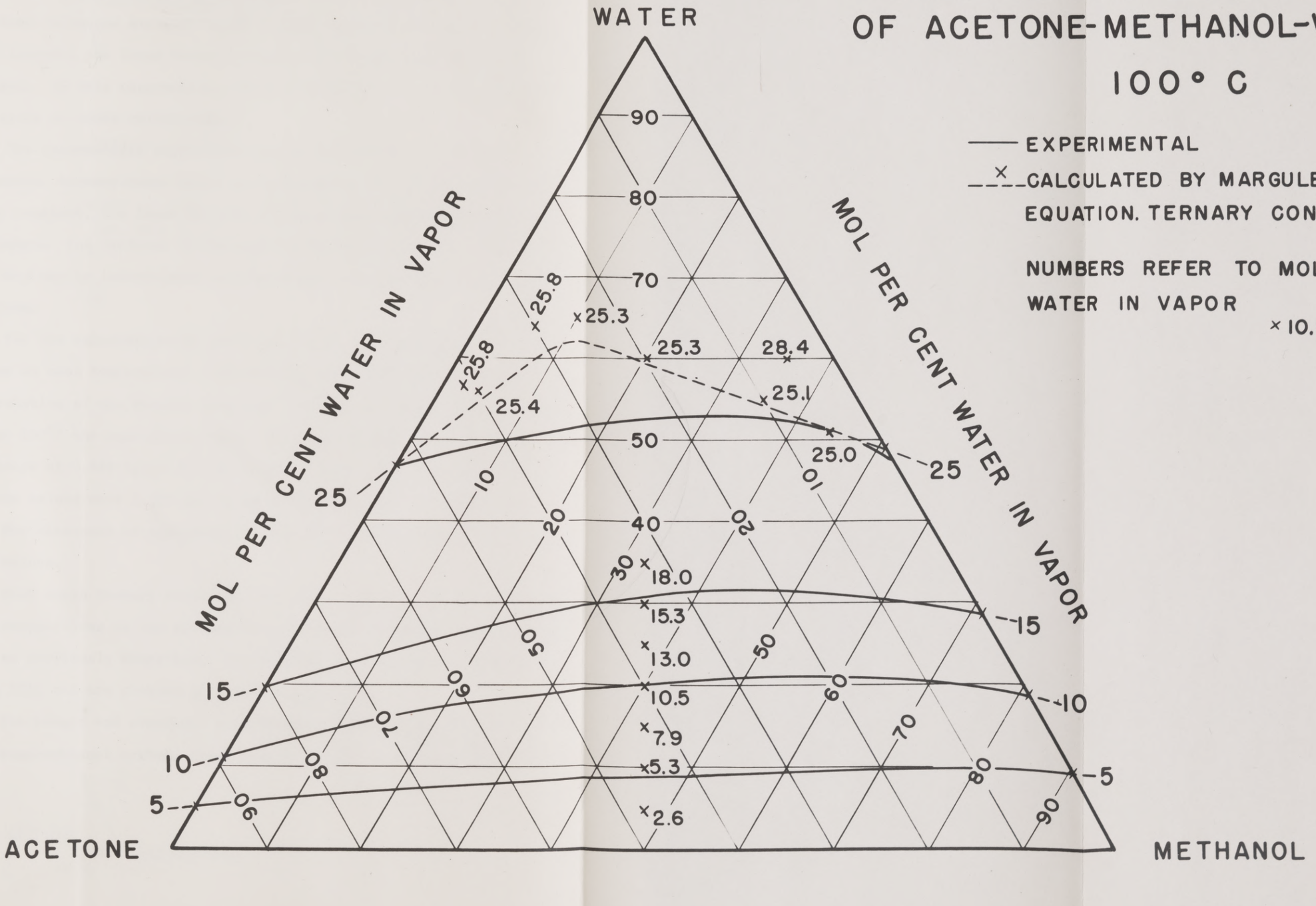
Examination of the ternary data at 100°C and 250°C and those reported by Griswold and Buford (15) at 760 mm Hg. show that the lines of constant mol per cent acetone in the vapor were quite regular, and that these could be established with confidence at other temperatures from binary data for acetone-water and acetone-methanol. One or two experimental points are sufficient to check their general consistency.

Having established general limits to the Margules ternary equations for the present system, the equations could be used to determine the water isoforms up to about 30 mol per cent water in the liquid phase. Isoforms in the intermediate and high water concentrations remain to be

FIGURE 27

MARGULES EQUATION VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

100° C



—— EXPERIMENTAL

_ _ × _ _ CALCULATED BY MARGULES 3-SUFFIX EQUATION. TERNARY CONSTANT C = 0.504

NUMBERS REFER TO MOL PER CENT WATER IN VAPOR

× 10.5

established. From the experimental data, it was observed that the isoforms tend to become straight lines as they approach the water corner of the diagram, the lines becoming straighter as the temperature is increased. By this observation, these isoforms may be drawn and confidence given to their reliability.

The intermediate region must now be considered. With the experimental ternary point which was required in the evaluation of the ternary constant, the lower portion of this intermediate region can be established. The isoforms in the water corner may then be established since they may be interpolated between those at temperatures below and above them.

For the calculations at 150°C and 200°C, two experimental points were run at each temperature. Compositions were selected for suitability in calculation of the ternary constant. The results are given in Table XVI. At 150°C the calculated values for C were 0.950 and 0.965 with the average of 0.958 taken for use in Eqs. (33), (34), and (35). At 200°C the values were 1.118 and 1.153 with the average of 1.136 being used. The closeness of agreement in each set indicates the precision of the values.

With these ternary constants, the vapor compositions at arbitrary liquid compositions in the applicable range were calculated in the exact manner as previously described. The results are tabulated in Tables XXI and XXII and are plotted in Figures 28 and 29.

The binary end constants used were the experimental values. For the acetone-methanol system, these constants were those determined at

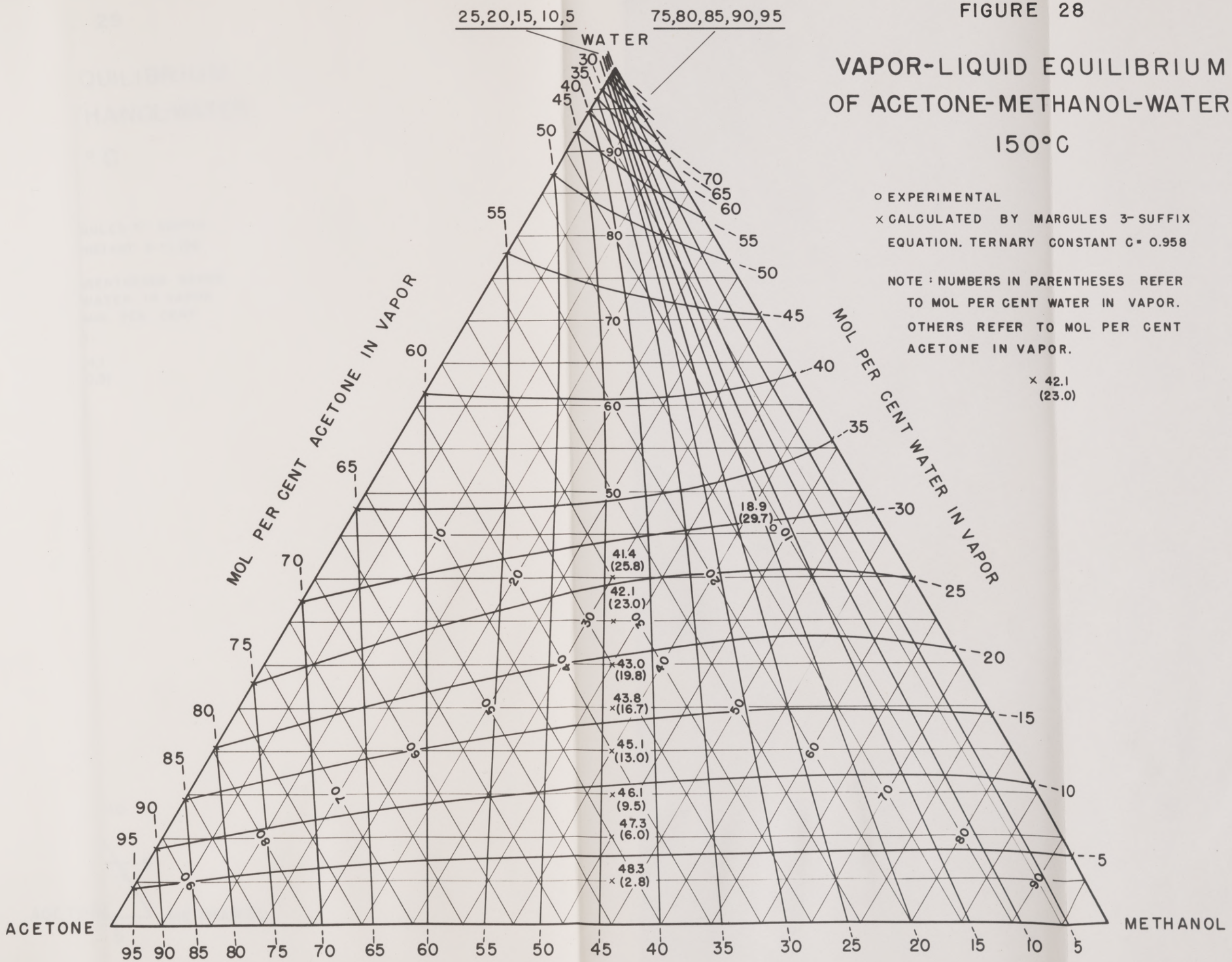


FIGURE 28

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER 150°C

○ EXPERIMENTAL

× CALCULATED BY MARGULES 3-SUFFIX EQUATION. TERNARY CONSTANT C = 0.958

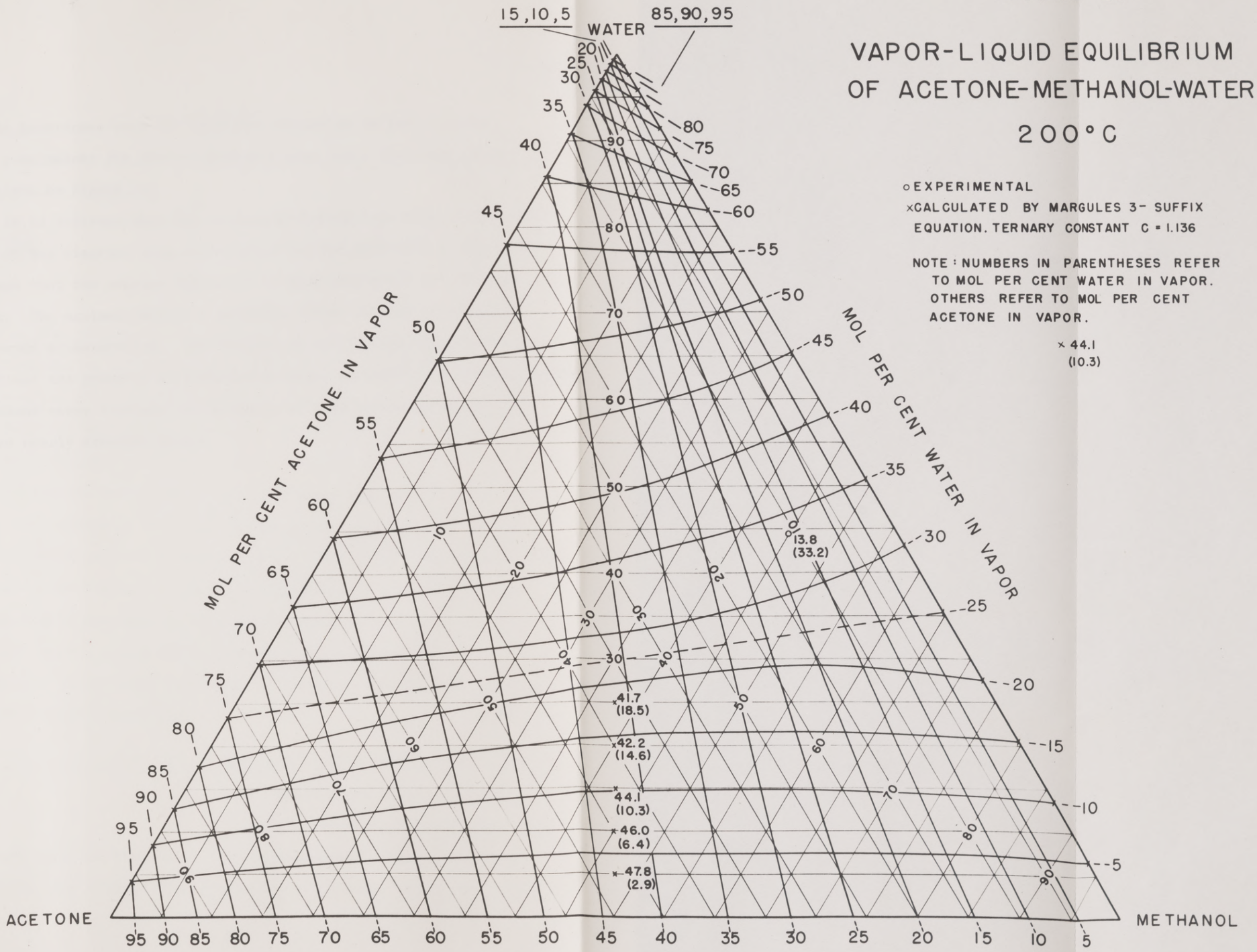
NOTE : NUMBERS IN PARENTHESES REFER TO MOL PER CENT WATER IN VAPOR. OTHERS REFER TO MOL PER CENT ACETONE IN VAPOR.

× 42.1
(23.0)

FIGURE 29

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

200°C



○ EXPERIMENTAL

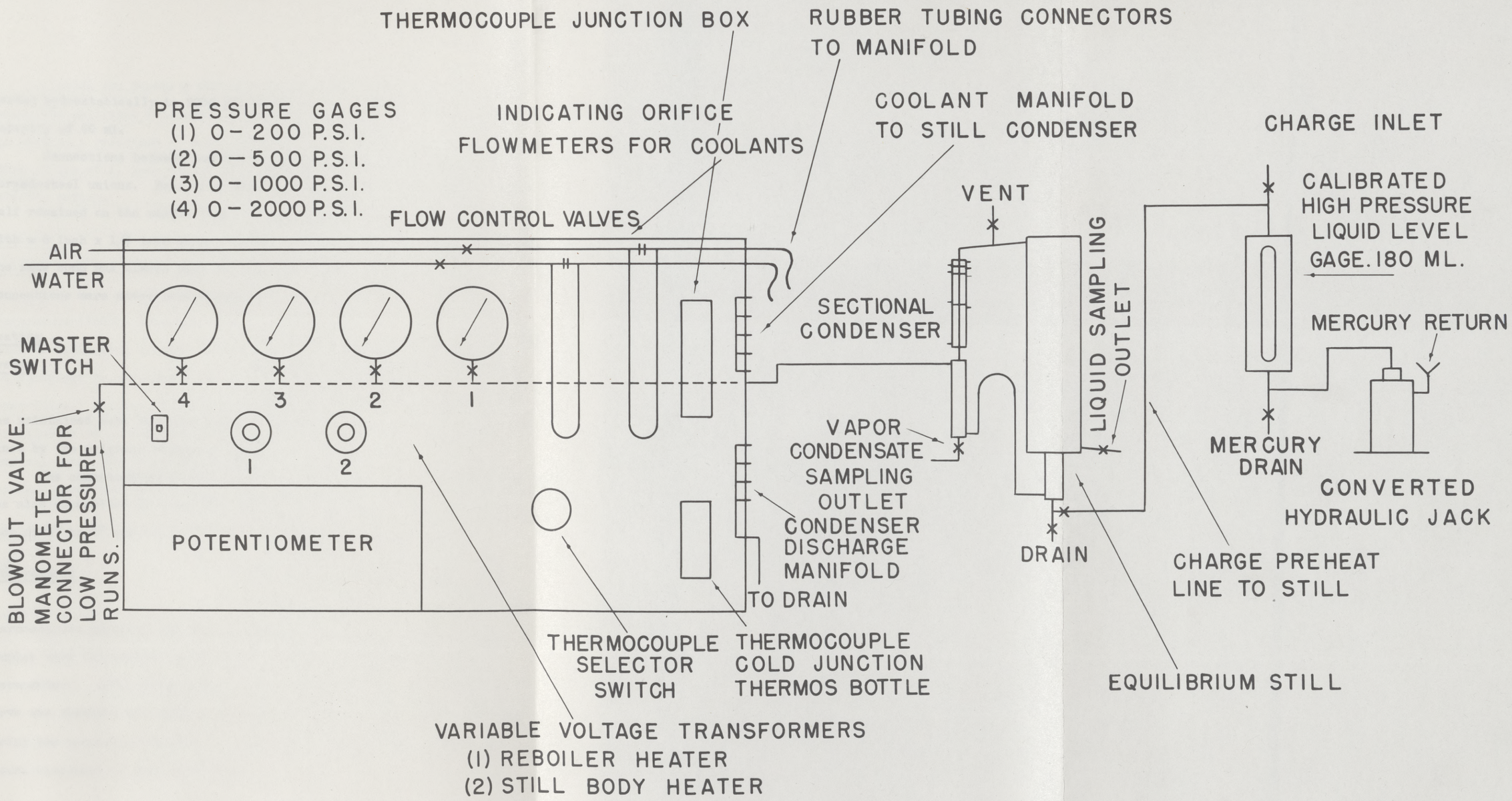
× CALCULATED BY MARGULES 3- SUFFIX EQUATION. TERNARY CONSTANT C = 1.136

NOTE: NUMBERS IN PARENTHESES REFER TO MOL PER CENT WATER IN VAPOR. OTHERS REFER TO MOL PER CENT ACETONE IN VAPOR.

× 44.1
(10.3)

100°C in accordance with the previous discussion on this system. Binary y--x points for acetone-methanol were taken from the average curve given on Figure 16.

It is believed that the maximum deviation from true equilibrium values of the diagrams thus constructed are not more than ± 2 mol per cent, and that the average deviation is approximately 1 mol per cent or less. The maximum deviation probably occurs at some intermediate water vapor concentration. The results in the low and high water concentrations are probably as accurate as could be determined experimentally. The acetone vapor isoforms are probably of even better accuracy since they are nearly straight lines.



SCHEMATIC DIAGRAM OF HIGH PRESSURE VAPOR-LIQUID EQUILIBRIUM APPARATUS

FIGURE 30

tested hydrostatically to 2000 psi before use. A finished bomb had a capacity of 60 ml.

Connections between bombs and sample lines were made by means of forged-steel unions. Half of a union was left on a bomb while the other half remained on the sample line. The other end of the bomb was fitted with a 6 inch x 1/4 inch copper tubing drain to facilitate sample removal. The same bomb was always used for the same still sample so that union connections were never interchanged.

Heating System — Heat input to the reboiler of the still was controlled by a variable-voltage transformer. The rate of heat input was maintained such that the still operated well within the limits determined by the original designers (14).

The compensating heater on the still body (to prevent refluxing) was also controlled by a variable-voltage transformer. A slight superheat of 3° to 5° was maintained on the vapor space in the still.

Temperatures — Vapor and liquid temperatures were measured by calibrated iron-constantan thermocouples inserted into the thermowells in the still. The thermocouples were calibrated against U. S. Bureau of Standards certified thermometers. After calibration and placing, the pressure-temperature curve was observed for water as a check. Periodic checks were also made during the course of the entire investigation by the above method to assure constancy of the calibration.

A Leeds and Northrup Portable Precision Potentiometer was used to obtain the millivolt readings. A crushed-ice slurry in a Dewar flask was used as a reference or cold junction. All thermocouples, including those on the still body walls, were connected to a multiple-junction selector switch.

Condenser Coolants — Air and water were used as coolants to the sectional condenser of the still. Water was used only on the lowest temperature (100°C) determinations. Flow control of the coolants was by means of indicating orifice flowmeters. Changes from one section of the condenser to the others when needed were rapidly made by manifold connections. Pressure fluctuations in the water supply necessitated installation of an overflow-type constant heat device. This assured constant water flow rates at all times. Minor fluctuations in air pressure were readily corrected by adjustment of the flow control valve.

Pressure Gages — To obtain maximum accuracy at all pressure ranges, four Bourdon-type pressure gages were used. For the low pressure determinations at 100°C, a mercury U-tube manometer was used. The gages used were Ashcroft Duragages in the following ranges:

Range, psi	Division, psi
0 to 200	2
0 to 500	5
0 to 1000	10
0 to 2000	20

All gages were calibrated with a deadweight tester, before, during, and after the experimental determinations. No significant changes were noted in any of the calibrations. Additional checks were obtained by the thermocouple checking of the vapor pressure of water.

All pressure connections were made by 3/16 inch stainless steel tubing with high pressure Ermeto fittings. Hoke brass needle-type valves were used to cut off gages not in use.

Charging System

A high-pressure charging system was installed to reduce the down time between runs. This permitted the introduction of controlled amounts of additional material to the still immediately after a run was completed, while the apparatus was still hot and under pressure.

A hydraulic automobile jack was converted to pump mercury by drilling and bolting the movable ram with a 1/4 inch machine bolt. The top was then drilled and tapped for 1/8 inch standard pipe thread for a tubing connector.

The required amount of material was charged into the still from a calibrated Jerguson high-pressure transparent liquid level gage, by displacement with mercury pumped by the converted jack. The capacity of the Jerguson gage reservoir was 160 ml. Its maximum operating pressure at room temperature was 1000 psi.

To preheat the charge and thus reduce the time required to attain the desired operating temperature, the line from the gage reservoir to the still was wrapped with about 15 feet of 21 gauge nichrome wire which

was insulated from the tubing with Fiberglas tape.

The system was readied for subsequent charging by simultaneously introducing more material to the reservoir as the mercury was drained by gravity flow back into the jack.

IV

OPERATIONS

The still was evacuated by means of a water aspirator prior to charging. A charge of approximately 400 to 450 ml of the desired composition was made up and introduced into the still through the liquid sampling outlet. Smaller charges were used at the higher temperatures so that the liquid level in the still remained within the recommended operating limits at equilibrium temperatures. After charging, heat was applied to the reboiler, and then to the compensating heater as soon as boiling commences. The system was then taken up to its operating temperature range. At this point, the pressure lines to the gages were purged of entrapped air by bleeding off a small quantity of the still vapors. The vent valve on the still was cracked momentarily to eliminate air trapped in the vapor space of the still itself.

The still was then brought under temperature control. Heat input into the reboiler was set to operate the still in the middle of the recommended distillation rate limits. The temperature and pressure were controlled by adjusting the rate of coolant flow to the operating section of the condenser.

After the still had been in operation and on constant temperature for about 30 minutes, small quantities of the liquid phase and of the vapor condensate were carefully bled out through the sampling valves to purge the sampling lines. This procedure might not have been necessary, but it served as an additional precaution that the samples were representative.

In all determinations, the still was operated for a sufficient time to insure a minimum charge turnover of one and one half times the charged volume on temperature. At least one hour was allowed to ascertain that the temperature was true and steady, then whatever additional time was required to provide the minimum charge turnover. In all of the determinations, total turnover was greater than the recommended minimum.

After equilibrium conditions were established as above, vapor condensate and liquid samples were taken. Preparatory to sampling, the double-valved sample bombs were thoroughly blown out and dried by compressed air. The air was dried through a 6-inch calcium chloride tube (with glass wool plugs on both ends), and was then filtered through a 5-inch cotton-filled tube. The bombs were connected to the still by their unions and were then evacuated by means of an aspirator. A suction flask with side arm was used as a trap for the aspirator. After evacuation, the drain tubes on the bombs were protected by slipping rubber tubing sections over their entire lengths to keep them dry during subsequent operations.

The vapor condensate and liquid sampling valves were simultaneously opened wide and then immediately shut after the samples were taken. Total sampling time averaged less than 10 seconds. Immediately after the samples were taken and the bomb valves closed, the bombs and contents were chilled with ice water while still in place. This cooled the bombs so that they could be handled, but more important, it reduced the pressure immediately so that the danger of leaks through possible faulty closure of the valves was minimized.

The bombs were then disconnected from the still. The union ends of the bombs were then thoroughly blown out with dry, clean, compressed air. To avoid changes in composition by vaporization during removal of the samples from the bombs for analysis, the bombs and contents were thoroughly chilled by placing them for about 10 minutes on a block of ice. Ice blocks rather than chips were used to avoid getting any water in the sample connections, as only the bombs' bodies were then in contact with the ice.

After chilling, the bombs were wiped dry. The rubber tubing protectors were removed from the drain tubes. The union ends of the bombs were again thoroughly blown out with clean, dried compressed air. The samples were removed for analysis after bleeding out and rejecting about 10 ml. of the contents to purge the drain tubes. The bombs were immediately dried by clean, dry air. They were dried again immediately before use.

While the bombs were chilling on the ice blocks, the cell was recharged for the next run, displacing the charge into the cell by mercury from the pump. Each successive charge was approximately 130 ml. in volume, since this was the total sample volume removed per determination. After charging was completed, a small quantity of the still vapors was bled through the vent valve to eliminate any air which might have been introduced during the charging.

The still was periodically drained and a completely fresh charge put in. On the average, a totally new charge was used every four or five runs. At the higher temperatures three to four runs was the average.

The period that the still was coming up to the desired operating temperature was utilized to analyze samples. This was done immediately after removing the samples from the bombs.

The temperatures in the liquid phase were observed an average of three to four times per minute. This was done to insure correct operating temperatures at all times and to adjust any variations due to fluctuations of voltage or coolant rates. For all runs the temperatures were maintained to within ± 0.005 millivolts of the required potentiometric reading during the entire time of the equilibrium run. This to less than ± 0.1°C.

To obtain maximum accuracy in the pressure readings, a knife edge was placed between gage divisions to aid in estimating fractions of a division.

Special precautions were used to maintain anhydrous conditions during the determinations on acetone-methanol. A 600 ml. storage reservoir was constructed from pipe fittings and connected directly to the Jerguson gage reservoir by means of stainless steel tubing. The large reservoir was vented through a valve to which a calcium chloride drying tube was connected. The purpose was to reduce the number of times a reagent bottle had to be opened and its contents exposed to the atmosphere. By opening the bottle once and swiftly pouring a sufficient quantity for three or four runs, the material was exposed only for a very short time. No bottle was ever exposed more than twice. On charging the Jerguson gage reservoir, the vent valve was opened, admitting dried air from the calcium chloride tube. After charging, the valve was shut.

VII

ANALYTICAL PROCEDURES

The analytical data reported by Griswold and Buford (15) were used in this work. For the acetone-water and methanol-water systems, densities were used in the analyses. For high concentrations of water (above 95 mol per cent), refractive indices were used for greater accuracy. Viscosity and surface tension effects limit the sensitivity of the density determination.

For the acetone-methanol system, refractive index alone was used for analysis.

Density and refractive index were used for the ternary system.

Refractive index was taken on a Bausch and Lomb Precision Oil Refractometer using monochromatic sodium light. The reproducibility of the reading is ± 0.00003 index units. Prism temperatures were maintained at 25°C ± 0.05°C. by a Constant Temperature Circulator manufactured by the Precision Scientific Company. Calibration of the refractometer was checked periodically by standard test pieces supplied by the manufacturer. Since the refractive indices were all in the lower range of the scale, double-distilled water was used to re-check the instrument's accuracy in this range. Large deviations, when observed, were corrected immediately by recalibration of the instrument with the standard test pieces.

Great care was taken to eliminate analytical errors. The methanol used for cleaning the prisms tended to condense extraneous water from the atmosphere as it evaporated and cooled the prism faces. To eliminate this, the prisms were carefully dried as much as possible after cleaning with

tissue. Then they were fanned for about a minute. This eliminated the possible presence of an adsorbed film of water.

Densities were determined by an apparatus similar to the one described by Osborne (30). The plummet was suspended from the arm of an Ainsworth type CL analytical balance by a length of 32 gauge nichrome wire made up in sections for greater flexibility. The sample was contained in a suitable size test tube supported on a sliding rack. The level of the constant temperature bath was maintained such that the test tube and sample were well immersed. The samples were protected from the atmosphere by tight fitting rubber stoppers protected by tin foil. After thermal equilibrium was established, the apparent weight of the plummet in the sample was determined. The density was then calculated using the calibration data on the plummet.

For all samples, including the calibration determinations, the same depth of liquid was used in order that the plummet and wire be immersed to the same depth. Periodic calibrations using distilled water were made to certify the true weight of the plummet.

Temperature control on the bath was by means of a mercury-in-glass thermoregulator. The temperature was maintained at 25°C ± 0.10°C. Density determinations are accurate to within 0.0001 unit.

Dryness of the plummet was assured by immersing it in acetone after each determination. The plummet was then dried by a dry, clean, lintless cloth. After it was returned to the balance hook, it was fanned for about a minute. This procedure was necessary to be sure that all the water was removed before the following determination.

VIII

PURIFICATION OF MATERIALS

Analytical reagent grade acetone and C. P. anhydrous methanol used in this research were obtained from the Mallinckrodt Chemical Works and the General Chemical Company, respectively. Before use, they were purified by distillation in a four-foot column packed with glass helices, using a reflux ratio of about eight to one. Heart cuts of 80 per cent by volume were retained for use, the first and last 10 per cent being discarded.

Refractive index and density for acetone checked closely with those given by Griswold and Buford (15). Purity of the methanol was checked by density alone. Its refractive index could not be checked on the Bausch and Lomb refractometer using sodium light. The constants for the purified materials are,

		I. C. T. (22, 23)	Griswold, Buford (15)	Experimental
Acetone	n_D^{25}	1.35589	1.35591	1.35590
	d_4^{25}	0.7841	0.7838	0.7837
Methanol	d_4^{25}	0.7867	0.7870	0.7869

Distilled water was obtained from the laboratory supply.

In the purification of the acetone and the methanol for use in the acetone-methanol determinations, great care was taken to obtain and maintain the materials in anhydrous condition. The acetone was dried for

several days over calcium chloride and the methanol was dehydrated with magnesium metal filings before distillation. The materials were collected in a flask which was suitably vented through a calcium chloride drying tube. A mercury seal was used to connect the receiver flask to the product take-off tube on the column head. The materials were stored in amber bottles and tightly capped. Toy ballons were used as tight-fitting rubber coverings over the capped bottles.

IX

SUMMARY OF EXPERIMENTAL AND CALCULATED VALUES

Table I.

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-WATER

100° C.

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_W	Z_A	Z_W	γ'_A	γ'_W
1	16.1	9.02	0.33	8.961	1.000	1.049	0.999	9.400	0.999
2	16.4	10.9	0.40	8.187	0.998	1.049	0.999	8.588	0.997
3	17.0	11.8	0.45	8.270	1.025	1.048	0.999	8.667	1.024
4	18.9	20.7	0.80	9.073	1.028	1.045	0.998	9.481	1.026
5	32.5	54.5	4.8	6.864	1.057	1.029	0.992	7.044	1.048
6	35.5	61.3	8.2	4.924	1.018	1.024	0.991	5.042	1.009
7	40.4	63.2	10.8	4.386	1.113	1.018	0.989	4.465	1.120
8	38.7	63.7	9.8	4.667	1.059	1.020	0.989	4.760	1.047
9	44.5	70.5	22.0	2.646	1.145	1.013	0.987	2.680	1.130
10	46.4	71.5	30.8	1.998	1.300	1.010	0.986	2.018	1.282
11	46.5	71.9	31.6	1.963	1.300	1.010	0.986	1.983	1.282
12	48.4	72.7	39.7	1.644	1.491	1.008	0.985	1.657	1.469
13	49.7	74.6	52.6	1.308	1.812	1.006	0.985	1.316	1.785
14	50.4	74.7	48.0	1.455	1.668	1.005	0.984	1.462	1.641
15	51.8	80.1	69.5	1.108	2.299	1.004	0.984	1.112	2.262
16	50.7	81.4	71.5	1.071	2.251	1.005	0.984	1.076	2.215
17	52.2	82.3	74.2	1.074	2.436	1.003	0.984	1.077	2.397
18	52.6	83.7	77.1	1.059	2.547	1.003	0.983	1.062	2.504
19	53.3	87.8	85.4	1.017	3.030	1.001	0.983	1.018	2.978
20	53.5	94.6	94.4	0.995	3.509	1.001	0.983	0.996	3.449
21	53.4	97.2	97.1	0.992	3.507	1.001	0.983	0.993	3.447
22	53.5	97.8	97.7	0.994	3.481	1.001	0.983	0.995	3.422

Table II

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-WATER

150° C.

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_W	z_A	z_W	γ'_A	γ'_W
1	72.5	4.4	0.23	8.212	1.009	1.107	0.999	9.091	1.008
2	97.5	29.5	2.4	7.096	1.021	1.080	0.990	7.664	1.011
3	126.8	44.3	7.1	4.686	1.102	1.047	0.980	4.904	1.080
4	147.5	52.5	16.3	2.813	1.213	1.024	0.973	2.880	1.180
5	160.0	58.8	34.0	1.596	1.468	1.010	0.969	1.612	1.422
6	163.5	61.6	43.0	1.387	1.596	1.006	0.968	1.395	1.545
7	169.4	67.7	57.8	1.175	1.879	0.999	0.966	1.174	1.815
8	172.4	73.1	68.6	1.088	2.140	0.996	0.965	1.084	2.065
9	173.3	75.0	72.2	1.066	2.259	0.995	0.965	1.061	2.180
10	174.3	77.7	76.3	1.051	2.377	0.994	0.964	1.045	2.291
11	174.1	82.1	81.8	1.034	2.482	0.994	0.964	1.028	2.393
12	173.9	84.5	85.4	1.019	2.676	0.994	0.964	1.013	2.580
13	172.6	87.7	88.7	1.010	2.722	0.996	0.965	1.006	2.627
14	171.4	90.2	91.2	1.004	2.766	0.997	0.965	1.001	2.669
15	169.6	94.7	95.3	0.998	2.768	0.999	0.966	0.997	2.674
16	168.4	95.7	96.0	0.994	2.624	1.001	0.966	0.995	2.535
17	167.7	96.8	97.0	0.991	2.591	1.002	0.967	0.993	2.505

Table III

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-WATER

200° C.

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_W	Z A	Z W	γ'_A	γ'_W
1	232	1.60	0.13	6.951	1.014	1.181	0.999	8.209	1.013
2	235	2.45	0.22	6.371	1.019	1.178	0.999	7.505	1.018
3	264	13.6	1.82	4.794	1.029	1.155	0.989	5.537	1.018
4	274	18.4	2.50	4.910	1.018	1.006	0.986	4.939	1.004
5	312	26.8	4.5	4.516	1.060	1.108	0.975	5.004	1.034
6	351	35.4	9.2	3.277	1.107	1.065	0.964	3.490	1.067
7	396	45.5	22.6	1.938	1.235	1.016	0.951	1.969	1.175
8	417	50.2	36.2	1.407	1.444	0.993	0.945	1.397	1.364
9	421	51.7	39.3	1.348	1.486	0.988	0.944	1.332	1.403
10	427	54.0	44.6	1.258	1.573	0.982	0.942	1.235	1.482
11	434	57.5	51.2	1.186	1.677	0.975	0.940	1.156	1.576
12	439	59.5	55.1	1.153	1.756	0.970	0.938	1.118	1.647
13	440	64.8	63.4	1.094	1.877	0.969	0.938	1.060	1.761
14	443	66.5	65.9	1.088	1.930	0.966	0.937	1.051	1.808
15	442	72.2	73.5	1.056	2.057	0.967	0.937	1.021	1.927
16	440	74.3	75.8	1.049	2.073	0.969	0.938	1.016	1.944

Table III (Continued)

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_W	Z_A	Z_W	γ'_A	γ'_W
17	439	75.3	77.2	1.042	2.110	0.970	0.938	1.011	1.979
18	435	79.4	81.6	1.030	2.160	0.974	0.940	1.003	2.030
19	428	84.7	86.7	1.018	2.184	0.981	0.942	0.999	2.057
20	427	85.8	87.7	1.017	2.187	0.982	0.942	0.999	2.060
21	413	91.9	93.0	0.992	2.115	0.998	0.946	0.990	2.001
22	411	92.8	93.7	0.989	2.080	1.000	0.947	0.989	1.970
23	412	93.1	94.0	0.992	2.100	0.999	0.946	0.991	1.987
24	405	97.6	97.8	0.982	1.982	1.006	0.948	0.990	1.879
25	405	97.7	97.9	0.983	1.913	1.006	0.948	0.989	1.814

Table IV

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-WATER

250° C

Run No.	PSIA	Mol % Acetone	
		Vapor	Liquid
1	586	1.5	0.2
2	594	2.5	0.4
3	606	3.9	0.7
4	676	13.8	2.6
5	804	29.2	10.4
6	876	36.3	22.7
7	914	39.2	28.5
8	919	40.0	29.6
9	939	42.5	36.4
10	939	42.8	34.9
11	949	46.2	40.1
12	954	46.6	41.2
13	970	52.1	49.6
14	899	53.5	54.0
15	870	55.6	55.6
16	980	57.2	57.4
17	965	65.3	65.3

Table V

VAPOR-LIQUID EQUILIBRIUM OF METHANOL-WATER

100° C.

Run No.	PSIA	Mol % Methanol Vapor	Mol % Methanol Liquid	γ_M	γ_W	Z_M	Z_W	γ'_M	γ'_W
1	15.1	1.92	0.22	2.599	1.010	1.030	1.000	2.677	1.010
2	16.0	8.6	1.10	2.467	1.006	1.029	0.999	2.538	1.005
3	18.0	19.1	3.5	1.928	1.027	1.027	0.999	1.980	1.026
4	19.4	24.5	5.3	1.769	1.052	1.025	0.998	1.813	1.050
5	20.7	31.3	7.4	1.727	1.045	1.024	0.997	1.768	1.042
6	23.9	43.4	12.1	1.691	1.047	1.021	0.996	1.726	1.043
7	25.6	49.6	16.3	1.536	1.049	1.019	0.995	1.565	1.044
8	29.7	61.9	28.1	1.290	1.071	1.016	0.993	1.311	1.064
9	31.4	66.2	35.2	1.165	1.114	1.014	0.990	1.181	1.103
10	36.4	75.0	52.2	1.032	1.295	1.010	0.991	1.042	1.283
11	39.3	79.2	60.6	1.013	1.411	1.009	0.989	1.022	1.395
12	40.9	82.4	66.7	0.997	1.470	1.007	0.988	1.004	1.452
13	45.2	91.1	82.6	0.982	1.586	1.005	0.987	0.987	1.565
14	48.5	96.9	93.2	0.994	1.528	1.004	0.985	0.998	1.505
15	48.9	97.6	94.6	0.995	1.492	1.004	0.985	0.999	1.470
16	48.9	98.1	95.8	0.988	1.498	1.004	0.985	0.992	1.476

Table VI

VAPOR-LIQUID EQUILIBRIUM OF METHANOL-WATER

150° C.

Run No.	PSIA	Mol % Methanol Vapor	Mol % Methanol Liquid	γ_M	γ_W	Z_M	Z_W	γ'_M	γ'_W
1	73.3	6.0	0.90	2.472	1.007	1.076	0.999	2.660	1.006
2	79.0	13.5	2.2	2.407	1.013	1.073	0.997	2.583	1.010
3	85.7	21.3	4.4	2.068	1.023	1.069	0.994	2.211	1.017
4	93.9	28.6	7.9	1.810	1.055	1.065	0.992	1.821	1.046
5	114.9	45.9	18.6	1.423	1.107	1.053	0.984	1.498	1.089
6	139.7	61.0	37.4	1.143	1.261	1.038	0.976	1.186	1.231
7	148.6	66.2	45.9	1.075	1.346	1.032	0.973	1.109	1.310
8	160.4	73.1	57.8	1.018	1.481	1.025	0.969	1.043	1.435
9	177.4	83.2	74.8	0.990	1.714	1.014	0.963	1.004	1.650
10	193.5	92.9	89.3	1.010	1.861	1.003	0.958	1.013	1.783
11	194.5	94.3	91.3	1.008	1.847	1.003	0.957	1.011	1.768
12	196.5	96.0	93.6	1.011	1.780	1.002	0.956	1.013	1.702
13	197.7	97.2	95.3	1.011	1.718	1.001	0.956	1.012	1.642
14	199.2	98.2	96.9	1.013	1.688	1.000	0.955	1.013	1.612

Table VII

VAPOR-LIQUID EQUILIBRIUM OF METHANOL-WATER

200° C.

Run No.	PSIA	Mol % Methanol		γ_M	γ_W	Z_M	Z_W	γ'_M	γ'_W
		Vapor	Liquid						
1	236	3.20	0.49	2.647	1.019	1.180	0.998	3.123	1.017
2	245	7.5	1.68	1.908	1.023	1.176	0.995	2.244	1.018
3	259	12.6	3.20	1.776	1.036	1.170	0.990	2.078	1.026
4	280	19.6	5.9	1.618	1.059	1.160	0.984	1.877	1.042
5	300	27.2	9.8	1.451	1.074	1.151	0.978	1.670	1.050
6	341	38.9	17.2	1.343	1.115	1.130	0.967	1.518	1.078
7	390	51.4	29.7	1.176	1.196	1.105	0.953	1.299	1.140
8	442	63.2	46.9	1.038	1.359	1.077	0.938	1.118	1.275
9	476	71.3	59.5	0.993	1.494	1.059	0.928	1.052	1.386
10	510	79.6	72.0	0.983	1.649	1.039	0.918	1.021	1.514
11	558	92.6	90.3	0.997	1.887	1.010	0.904	1.007	1.706
12	560	92.7	90.5	0.999	1.907	1.009	0.903	1.008	1.722
13	565	94.5	93.5	0.994	1.834	1.006	0.902	1.000	1.654
14	569	96.2	94.7	1.007	1.808	1.003	0.901	1.010	1.629
15	572	97.4	96.3	1.008	1.767	1.002	0.900	1.010	1.590

Table VIII

VAPOR LIQUID EQUILIBRIUM OF METHANOL-WATER

250° C

Run No.	PSIA	Mol % Methanol	
		Vapor	Liquid
1	681	16.3	6.6
2	764	28.0	13.2
3	818	34.4	18.0
4	889	42.3	25.4
5	949	48.7	33.1
6	994	54.2	40.4
7	1049	59.6	48.3
8	1099	64.3	55.3
9	1159	69.8	63.1
10	1204	75.6	73.2
11	1219	77.2	77.2
12	1234	79.7	79.7

Table IX

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL

100° C.

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_M	Z_A	Z_M	γ'_A	γ'_M
1	51.1	7.0	4.7	1.412	0.984	1.005	1.003	1.419	0.987
2	51.7	9.3	6.8	1.312	0.992	1.004	1.002	1.317	0.994
3	54.3	18.7	14.6	1.290	1.020	1.000	1.002	1.290	1.022
4	55.0	25.8	22.0	1.197	1.032	0.999	1.002	1.196	1.034
5	58.2	41.7	39.7	1.134	1.110	0.995	1.000	1.128	1.110
6	58.4	50.7	50.7	1.083	1.152	0.995	1.000	1.078	1.152
7	58.4	54.7	56.2	1.054	1.191	0.995	1.000	1.049	1.191
8	58.4	59.8	62.4	1.038	1.232	0.994	1.000	1.032	1.232
9	58.2	61.4	64.1	1.043	1.218	0.995	1.000	1.038	1.218
10	58.3	63.5	66.0	1.041	1.234	0.995	1.000	1.036	1.234
11	57.4	71.1	74.7	1.014	1.293	0.996	1.001	1.015	1.294
12	55.9	81.9	87.0	0.973	1.535	0.998	1.001	0.971	1.537
13	54.4	91.7	95.2	0.972	1.855	1.000	1.002	0.972	1.859
14	53.4	95.0	97.7	0.963	2.290	1.001	1.002	0.964	2.294

Table X

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL

150° C.

Run No.	PSIA	Mol % Acetone Vapor	Mol % Acetone Liquid	γ_A	γ_M	Z_A	Z_M	γ'_A	γ'_M
1	205	8.3	7.4	1.359	1.017	0.960	0.996	1.305	1.013
2	205	10.7	9.8	1.328	1.009	0.960	0.995	1.275	1.004
3	206	13.8	13.2	1.274	1.026	0.959	0.995	1.222	1.021
4	206	18.1	17.6	1.257	1.031	0.958	0.995	1.204	1.026
5	207	22.8	22.8	1.226	1.039	0.958	0.995	1.174	1.034
6	206	30.4	31.9	1.164	1.058	0.958	0.995	1.115	1.053
7	204	37.8	41.2	1.110	1.085	0.961	0.996	1.067	1.081
8	202	44.1	48.1	1.098	1.093	0.963	0.998	1.057	1.091
9	199	51.5	58.1	1.046	1.158	0.966	1.000	1.010	1.158
10	194	63.5	71.5	1.018	1.244	0.972	1.003	0.989	1.248
11	190	69.5	77.8	1.003	1.307	0.977	1.006	0.980	1.315
12	183	77.6	86.1	0.979	1.483	0.983	1.010	0.962	1.498
13	178	85.0	93.4	0.961	2.034	0.989	1.013	0.950	2.060
14	174	89.6	96.5	0.959	2.600	0.944	1.015	0.953	2.639
15	169	96.5	99.1	0.972	3.290	1.000	1.020	0.972	3.356

Table XI

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL

200° C.

Run No.	PSIA	Mol % Acetone		γ_A	γ_M	Z_A	Z_M	γ'_A	γ'_M
		Vapor	Liquid						
1	578	8.3	8.9	1.310	1.013	0.823	0.998	1.078	1.011
2	575	11.4	12.2	1.306	1.010	0.827	1.000	1.080	1.010
3	570	15.3	16.6	1.277	1.008	0.832	1.003	1.062	1.011
4	564	20.5	22.8	1.233	1.011	0.838	1.006	1.033	1.017
5	548	29.2	33.2	1.172	1.012	0.855	1.017	1.002	1.029
6	520	45.1	52.8	1.081	1.054	0.885	1.034	0.957	1.090
7	497	59.1	69.2	1.032	1.149	0.907	1.046	0.936	1.202
8	438	65.7	76.9	1.003	1.249	0.924	1.055	0.927	1.318
9	459	77.5	90.0	0.962	1.783	0.948	1.068	0.912	1.904
10	428	91.3	99.0	0.961	6.492	0.981	1.085	0.943	7.044

Table XII

CALCULATED VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL

150°C.

Mol % Acet. in Liquid	γ'_A	γ'_M	πq_A [a]	πq_M [a]	π [b]	Mol & Acet. in Vapor
10	1.29	1.00	22.6	179.7	202.3	11.2
20	1.19	1.02	41.9	163.3	205.2	20.4
30	1.12	1.06	59.3	148.6	207.9	28.5
40	1.07	1.09	75.4	130.9	206.3	36.6
50	1.04	1.14	91.5	114.1	205.6	44.5
60	1.02	1.19	107.4	95.8	203.2	52.8
70	1.00	1.27	122.1	75.9	198.0	61.6
80	1.00	1.38	139.0	54.8	193.8	71.7
90	1.00	1.58	154.9	31.2	186.1	83.2

[a] From relation, $\pi y = \gamma' P x / Z$

[b] From relation, $\pi = \pi y_A + \pi y_M$

Table XIII

CALCULATED VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL

200° C.

Mol % Acet. in Liquid	γ'_A	γ'_M	π^0_A	π^0_M	π	Mol % Acet. in Vapor
10	1.24	1.00	62.1	518.7	581	10.7
20	1.14	1.02	114.5	471.3	586	19.5
30	1.06	1.06	159.8	428.1	588	27.2
40	1.01	1.09	199.9	374.7	575	34.8
50	1.00	1.14	246.9	326.3	573	43.1
60	1.00	1.19	293.4	271.1	564	52.0
70	1.00	1.27	337.5	215.5	553	61.0
80	1.00	1.38	372.6	152.4	525	71.0
90	1.00	1.58	401.5	86.1	488	82.4

Table XIV

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

100° C.

Run No.	PSIA	Vapor Comp. Mol % A	M	W	Liquid Comp. Mol % A	M	W	γ_A	γ_M	γ_W
1	55.4	32.3	64.8	2.9	27.0	67.9	5.1	1.230	1.043	2.143
2	54.6	90.1	6.9	3.1	91.6	5.0	3.4	0.996	1.486	3.386
3	56.9	62.1	33.9	4.0	60.7	33.0	6.3	1.080	1.153	2.458
4	56.5	43.0	52.5	4.5	38.1	54.9	7.0	1.181	1.064	2.466
5	54.4	32.4	62.1	5.5	25.7	64.0	10.3	1.272	1.041	1.976
6	52.9	31.1	62.4	6.5	23.1	63.9	13.0	1.321	1.019	1.799
7	54.6	45.5	47.4	7.1	38.5	47.9	13.6	1.197	1.066	1.939
8	51.0	25.9	65.7	8.4	17.7	65.4	16.9	1.384	1.010	1.724
9	50.5	27.2	62.9	9.9	18.2	61.6	20.2	1.400	1.017	1.604
10	53.4	59.3	29.5	11.2	49.4	29.4	21.2	1.189	1.057	1.919
11	49.9	32.0	55.8	12.2	20.1	54.9	25.0	1.474	1.000	1.656
12	50.2	33.9	53.5	12.6	19.0	54.6	26.4	1.662	0.968	1.630
13	53.6	80.8	6.4	12.8	77.0	5.9	17.1	1.044	1.147	2.729
14	49.4	36.8	48.9	14.3	22.0	47.8	30.2	1.533	0.997	1.591
15	52.9	76.3	7.7	16.0	67.2	8.2	24.6	1.114	0.980	2.340
16	51.3	54.1	29.6	16.3	37.9	29.9	32.2	1.358	1.002	1.766
17	49.2	47.1	33.9	19.0	27.5	34.4	38.1	1.563	0.956	1.669
18	51.2	66.1	14.5	19.4	46.0	17.1	36.9	1.355	0.856	1.831
19	45.4	30.8	49.5	19.7	14.4	44.0	41.6	1.802	1.007	1.462
20	42.1	18.7	59.3	22.0	7.5	47.0	45.5	1.947	1.048	1.385

Table XIV (Continued)

Run No.	PSIA	Vapor Comp. Mol % A	M	W	Liquid Comp. Mol % A	M	W	γ_A	γ_M	γ_W
21	49.8	69.4	8.4	22.2	44.4	13.0	42.6	1.444	0.635	1.765
22	46.5	52.9	22.9	24.2	25.2	24.3	50.5	1.811	0.864	1.516
23	48.4	66.6	8.7	24.7	36.1	12.7	51.2	1.657	0.654	1.588
24	42.1	29.4	44.3	26.3	10.3	34.5	55.2	2.229	1.066	1.364
25	43.7	43.6	30.1	26.3	16.7	28.7	54.6	2.117	0.904	1.426
26	45.2	58.6	13.5	27.9	23.2	16.0	60.8	2.118	0.752	1.411
27	40.6	27.5	44.2	28.3	9.1	33.8	57.1	2.276	1.047	1.369
28	43.4	51.6	19.9	28.5	17.8	21.3	60.9	2.330	0.800	1.382
29	44.5	65.8	4.1	30.2	21.5	3.3	75.2	2.527	1.090	1.216
30	41.4	42.7	26.7	30.6	12.8	23.3	63.9	2.562	0.936	1.349
31	42.4	58.9	9.2	31.9	15.8	8.8	75.4	2.932	0.874	1.220
32	40.0	41.1	26.1	32.8	10.0	19.3	70.7	3.050	1.067	1.262
33	39.9	50.3	15.6	34.1	11.9	11.9	76.2	3.129	1.032	1.211
34	36.5	32.5	31.7	35.8	6.9	19.8	73.3	3.190	1.153	1.213
35	38.4	46.8	16.7	36.5	8.9	13.1	78.0	3.746	0.966	1.222
36	34.4	21.2	41.9	36.9	4.3	22.5	73.2	3.161	1.264	1.180
37	32.5	20.8	41.1	38.1	3.3	20.4	76.3	3.800	1.291	1.104
38	35.4	41.2	19.7	39.1	6.6	11.9	81.5	4.100	1.156	1.155
39	31.4	19.7	39.6	40.7	2.8	18.2	79.0	4.099	1.348	1.100
40	28.9	24.8	27.1	48.1	2.4	10.7	86.9	5.540	1.444	1.088

Table XIV (Continued)

Run No.	PSIA	Vapor Comp. Mol % A	M	W	Liquid Comp. Mol % A	M	W	γ_A	γ_M	γ_W
41	29.2	35.5	13.2	51.3	3.1	4.8	92.1	6.204	1.584	1.106
42	28.8	39.5	9.1	51.4	3.1	3.8	93.1	6.808	1.360	1.082
43	25.6	28.7	14.8	56.5	1.9	4.4	93.7	7.174	1.698	1.050
44	24.6	31.4	9.8	58.9	1.9	2.9	95.2	7.543	1.640	1.035
45	23.7	25.6	12.6	61.8	1.5	3.4	95.1	7.475	1.732	1.048
46	22.6	18.2	14.6	67.2	0.8	4.0	95.2	9.539	1.627	1.085
47	21.8	28.1	2.7	69.2	1.0	1.8	97.2	11.365	0.645	1.056
48	20.9	16.4	11.2	72.4	0.7	3.1	96.2	9.084	1.489	1.070
49	21.3	21.0	5.4	74.6	0.9	2.3	96.8	9.221	0.986	1.118
50	19.4	6.9	17.5	75.6	0.1	3.9	96.0	2.483	1.674	1.039
51	17.9	11.0	4.5	84.5	0.1	1.8	98.1	---	0.883	1.049

Table XIV (Continued)

Run No.	Z_A	Z_M	Z_W	γ'_A	γ'_M	γ'_W	R_A	R_M	R_W
1	0.998	1.001	0.982	1.228	1.044	2.104	7.0	15.9	28.5
2	1.000	1.002	0.983	0.996	1.489	3.328	40.5	3.6	94.8
3	0.996	1.001	0.981	1.076	1.154	2.411	16.0	9.4	64.8
4	0.996	1.001	0.982	1.176	1.065	2.422	11.3	15.5	41.0
5	1.000	1.002	0.983	1.272	1.043	1.942	13.9	28.6	28.6
6	1.002	1.002	0.983	1.324	1.021	1.768	16.9	36.0	26.6
7	1.000	1.002	0.983	1.197	1.068	1.906	22.1	26.1	44.6
8	1.005	1.003	0.984	1.391	1.013	1.696	20.5	48.8	21.3
9	1.005	1.003	0.985	1.407	1.020	1.580	24.7	52.6	22.8
10	1.001	1.002	0.983	1.190	1.059	1.886	41.9	30.0	62.7
11	1.006	1.003	0.985	1.483	1.003	1.631	31.3	55.4	26.8
12	1.006	1.003	0.985	1.672	0.971	1.606	32.6	58.1	25.8
13	1.001	1.002	0.983	1.045	1.149	2.682	74.3	18.2	92.9
14	1.007	1.003	0.985	1.544	1.000	1.567	38.7	57.8	31.5
15	1.002	1.002	0.983	1.116	0.982	2.300	75.0	26.8	89.1
16	1.004	1.003	0.984	1.363	1.005	1.738	51.8	45.9	55.9
17	1.007	1.003	0.985	1.574	0.959	1.644	52.6	58.1	44.4
18	1.004	1.003	0.984	1.370	0.858	1.802	68.3	44.5	72.9
19	1.010	1.005	0.987	1.820	1.012	1.443	48.6	74.3	24.6
20	1.016	1.007	0.988	1.978	1.055	1.368	49.2	85.8	13.8

Table XIV (Continued)

Run No.	Z_A	Z_M	Z_W	γ'_A	γ'_M	γ'_W	R_A	R_M	R_W
21	1.006	1.003	0.984	1.453	0.637	1.738	76.6	49.0	77.4
22	1.010	1.005	0.986	1.829	0.868	1.495	67.5	66.7	50.9
23	1.008	1.003	0.985	1.670	0.656	1.564	80.1	58.6	74.0
24	1.016	1.007	0.988	2.265	1.073	1.348	61.5	84.3	23.0
25	1.014	1.004	0.987	2.147	0.908	1.407	65.5	76.6	36.8
26	1.012	1.005	0.987	2.143	0.756	1.393	79.2	72.4	59.2
27	1.018	1.008	0.989	2.317	1.055	1.354	62.8	86.2	21.2
28	1.014	1.006	0.987	2.363	0.805	1.364	74.1	77.4	45.5
29	1.013	1.006	0.987	2.560	1.096	1.200	81.2	77.8	86.7
30	1.017	1.007	0.988	2.606	0.942	1.333	73.3	83.3	35.4
31	1.015	1.006	0.988	2.976	0.879	1.205	89.5	82.7	64.2
32	1.019	1.008	0.989	3.108	1.076	1.248	78.6	87.6	34.1
33	1.019	1.008	0.989	3.188	1.040	1.198	86.5	86.5	50.0
34	1.023	1.010	0.990	3.263	1.164	1.201	78.7	91.4	25.8
35	1.021	1.009	0.990	3.825	0.975	1.210	85.6	89.8	40.4
36	1.026	1.012	0.991	3.243	1.279	1.169	76.5	94.4	16.0
37	1.028	1.013	0.992	3.906	1.308	1.095	78.9	95.9	13.9
38	1.024	1.011	0.991	4.198	1.169	1.145	87.2	92.5	35.7
39	1.030	1.014	0.993	4.222	1.367	1.092	81.3	96.6	13.3
40	1.033	1.016	0.994	5.723	1.467	1.081	89.0	97.3	18.3

Table XIV (Continued)

Run No.	Z_A	Z_M	Z_W	γ'_A	γ'_M	γ'_W	R_A	R_M	R_W
41	1.033	1.016	0.994	6.409	1.609	1.099	95.0	96.7	39.2
42	1.033	1.016	0.994	7.033	1.382	1.076	96.1	96.8	44.9
43	1.038	1.019	0.995	7.447	1.730	1.045	95.5	98.1	30.2
44	1.039	1.020	0.996	7.837	1.673	1.031	97.0	98.0	39.6
45	1.039	1.021	0.996	7.766	1.768	1.044	96.5	98.4	30.6
46	1.041	1.022	0.997	9.930	1.663	1.082	96.0	99.2	16.7
47	1.042	1.023	0.997	11.842	0.660	1.053	98.2	99.0	35.7
48	1.043	1.024	0.997	9.475	1.525	1.067	96.9	99.3	18.4
49	1.043	1.023	0.997	9.618	1.009	1.115	97.7	99.1	28.1
50	1.045	1.025	0.998	2.595	1.716	1.037	96.1	99.9	2.5
51	1.046	1.027	0.999	---	0.907	1.048	81.2	77.8	86.7

Table XV

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

250° C.

Run No.	PSIA	Vapor Comp., Mol % A	M	W	Liquid Comp., Mol % A	M	W
1	1189	1.7	72.6	25.7	1.5	69.4	29.1
2	1184	1.6	72.2	26.2	1.5	67.8	30.7
3	1134	6.9	65.1	28.0	6.9	65.1	28.0
4	1154	5.5	64.9	29.6	5.5	64.0	30.5
5	1154	3.8	65.7	30.5	3.8	60.6	35.6
6	1114	7.2	58.7	34.1	6.5	54.2	39.3
7	1109	9.2	56.5	34.3	8.9	55.3	35.8
8	1114	5.2	60.5	34.3	4.7	53.7	41.6
9	1079	17.1	45.7	37.2	17.2	45.7	37.2
10	1064	15.9	45.2	38.9	15.6	44.7	39.7
11	1069	7.7	52.5	39.8	6.2	45.4	48.4
12	1060	13.1	46.6	40.3	11.5	42.1	46.4
13	1044	26.3	32.1	41.6	25.8	32.2	42.0
14	1052	10.9	47.5	41.6	9.4	41.4	49.2
15	1034	35.1	21.9	43.0	32.8	21.3	45.9
16	969	46.0	10.7	43.3	46.0	10.7	43.3
17	1030	27.5	28.7	43.8	26.3	26.9	46.8
18	1020	41.3	14.6	44.1	40.5	13.9	45.6
19	1020	39.6	15.9	44.5	39.6	15.9	44.5
20	1024	35.5	19.8	44.7	34.8	19.4	45.8

Table XV (Continued)

Run No.	PSIA	Vapor Comp., Mol % A	M	W	Liquid Comp., Mol % A	M	W
21	1010	11.4	43.0	45.6	9.4	36.8	53.8
22	1020	24.5	29.0	46.5	20.9	25.4	53.7
23	1000	11.2	42.1	46.7	8.5	34.0	57.5
24	1014	36.1	17.1	46.8	31.5	18.8	49.7
25	1010	32.7	19.7	47.6	29.2	18.3	52.5
26	990	9.9	42.1	48.0	7.3	32.8	59.9
27	974	15.5	34.0	50.5	11.7	27.4	60.9
28	974	22.9	26.3	50.8	18.0	22.5	59.5
29	974	32.3	16.6	51.1	28.7	15.2	56.1
30	959	46.5	2.2	51.3	45.8	2.2	52.0
31	974	42.8	5.7	51.5	40.4	4.8	54.8
32	974	38.8	9.0	52.2	34.0	7.9	58.1
33	959	23.3	23.9	52.8	16.4	21.3	62.3
34	960	31.0	14.9	54.1	24.0	12.3	63.7
35	954	18.8	26.8	54.4	12.3	20.1	67.6
36	954	35.5	8.9	55.6	28.4	7.7	63.9
37	954	25.0	19.2	55.8	17.2	15.2	67.6
38	934	28.6	11.9	59.5	19.2	8.4	72.4
39	909	17.6	22.7	59.7	10.1	14.6	75.3
40	904	22.4	16.8	60.8	12.9	10.7	76.4

Table XV (Continued)

Run No.	PSIA	Vapor Comp., Mol % A	M	W	Liquid Comp., Mol % A	M	W
41	900	23.7	14.8	61.5	13.7	9.4	76.9
42	868	15.3	20.3	64.4	7.4	11.6	81.0
43	854	10.9	23.9	65.2	4.4	13.9	81.7
44	857	20.4	13.9	65.7	10.2	8.0	81.8
45	848	19.2	14.5	66.3	8.8	8.4	82.8
46	819	16.7	13.2	70.1	6.7	6.7	86.6
47	821	20.2	9.0	70.8	8.2	4.9	86.9
48	794	9.9	18.3	71.8	2.9	9.9	87.2
49	784	18.8	6.4	74.8	6.2	3.3	90.5
50	769	10.6	14.4	75.0	3.0	7.3	89.7
51	767	14.3	9.5	76.2	4.3	4.9	90.8
52	752	9.1	14.4	76.5	2.5	7.2	90.3
53	732	5.9	15.4	78.7	1.2	7.4	91.4
54	739	14.0	6.1	79.9	3.6	3.1	93.3
55	714	11.8	7.1	81.1	3.0	2.9	94.1
56	699	5.7	10.7	83.6	1.2	4.2	94.6
57	689	6.0	9.2	84.8	1.0	3.9	95.1

Table XVI

TERNARY CONSTANTS CALCULATED BY

MARGULES THREE SUFFIX EQUATIONS

	PSIA	X_A	X_M	X_W	Y_A	Y_M	Y_W	γ'_A	γ'_M	γ'_W	C
100°C	45.4	0.144	0.440	0.416	0.308	0.495	0.197	1.820	1.012	1.443	0.502
	54.6	0.385	0.479	0.136	0.455	0.474	0.071	1.197	1.068	1.906	0.506
							Av. = 0.504				
150°C	167.1	0.110	0.432	0.457	0.182	0.521	0.297	1.640	1.031	1.522	0.950
	165.9	0.112	0.420	0.468	0.188	0.507	0.305	1.654	1.026	1.515	0.965
							Av. = 0.958				
200°C	482	0.106	0.449	0.445	0.138	0.523	0.339	1.411	1.032	1.506	1.118
	475	0.107	0.449	0.443	0.138	0.530	0.332	1.390	1.037	1.463	1.153
							Av. = 1.136				

Table XVII

TERNARY ACTIVITY COEFFICIENTS OF ACETONE

CALCULATED BY MARGULES THREE SUFFIX EQUATION

100° C C = 0.504

$$\text{Parameter} = R_A = 100 \frac{X_W}{X_W + X_M}$$

Mol Per Cent Acetone in Liquid

R_A	0	10	20	30	50	60	70	80	90
100	9.250	5.243	3.302	2.285	1.395	1.202	1.091	1.032	1.006
90	6.207	3.953	2.728	2.025	1.344		1.087		
80	4.457	3.106	2.331	1.834	1.305		1.084		
70	3.398	2.586	2.051	1.691	1.273		1.083		
60	2.734	2.217	1.851	1.585	1.252		1.080		
50	2.289	1.962	1.707	1.509	1.236		1.080		
40	1.991	1.781	1.602	1.451	1.224		1.080		
30	1.781	1.649	1.523	1.408	1.215		1.080		
20	1.626	1.549	1.462	1.373	1.208		1.080		
10	1.503	1.466	1.409	1.343	1.201		1.080		
0	1.395	1.392	1.362	1.314	1.194	1.134	1.080	1.038	1.010

Table XVIII

TERNARY ACTIVITY COEFFICIENTS OF METHANOL

CALCULATED BY MARGULES THREE SUFFIX EQUATION

100° C C = 0.504

Parameter = $R_M = 100 \frac{X_W}{X_W + X_A}$

Mol Per Cent Methanol in Liquid

R_M	0	10	20	30	50	60	70	80	90
100	2.765	2.048	1.620	1.356	1.094	1.037	1.008	0.998	0.998
90	1.893	1.553	1.332	1.189	1.040		0.998		
80	1.435	1.268	1.158	1.082	1.006		0.990		
70	1.206	1.120	1.058	1.019	0.985		0.985		
60	1.099	1.046	1.011	0.987	0.975		0.984		
50	1.078	1.033	1.004	0.986	0.979		0.985		
40	1.126	1.069	1.030	1.005	0.985		0.988		
30	1.241	1.150	1.087	1.044	1.001		0.995		
20	1.422	1.276	1.173	1.102	1.024		1.000		
10	1.682	1.448	1.288	1.177	1.053		1.008		
0	2.030	1.670	1.429	1.267	1.087	1.042	1.017	1.004	1.000

Table XIX

TERNARY ACTIVITY COEFFICIENTS OF WATER

CALCULATED BY MARGULES THREE SUFFIX EQUATION

100^{o} C C = 0.504

Parameter = $R_W = 100 \frac{X_A}{X_A + X_M}$

Mol Per Cent Water in Liquid

R_W	0	10	20	30	50	60	70	80	90
100	3.781	3.395	2.945	2.496	1.744	1.469	1.262	1.117	1.030
90	3.163	2.937	2.626	2.288	1.667		1.241		
80	2.727	2.562	2.380	2.117	1.600		1.223		
70	2.412	2.345	2.188	1.981	1.544		1.206		
60	2.179	2.150	2.036	1.869	1.494		1.190		
50	2.001	1.996	1.912	1.776	1.452		1.177		
40	1.860	1.872	1.809	1.696	1.413		1.164		
30	1.741	1.765	1.720	1.627	1.379		1.153		
20	1.637	1.669	1.640	1.564	1.348		1.142		
10	1.534	1.578	1.564	1.505	1.318		1.132		
0	1.430	1.487	1.488	1.446	1.290	1.202	1.122	1.058	1.016

Table XX

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

CALCULATED BY MARGULES THREE SUFFIX EQUATIONS

100° C C = 0.504

Liquid Comp., Mol %							Vapor Comp., Mol %	
A	M	W	γ'_A	γ'_M	γ'_W	π	A	W
47.5	47.5	5.0	1.218	1.065	2.010	58.5	53.6	2.6
45.0	45.0	10.0	1.244	1.044	1.996	57.1	53.1	5.2
42.5	42.5	15.0	1.275	1.024	1.962	55.8	52.5	7.9
40.0	40.0	20.0	1.312	1.007	1.912	54.4	52.0	10.5
37.5	37.5	25.0	1.355	0.993	1.849	53.1	51.5	13.0
35.0	35.0	30.0	1.410	0.985	1.776	51.9	51.1	15.3
20.0	20.0	60.0	2.179	1.101	1.302	46.0	50.5	25.3
17.5	17.5	65.0	2.450	1.165	1.236	45.1	50.6	26.5
5.0	44.0	51.0	2.224	1.079	1.308	39.7	14.8	25.0
10.0	35.0	55.0	2.355	1.089	1.297	42.3	29.5	25.0
25.0	10.0	65.0	2.313	1.144	1.280	49.2	63.0	25.3
40.0	4.0	56.0	1.639	1.068	1.521	50.0	70.3	25.4
41.0	2.0	57.0	1.640	1.078	1.520	50.0	72.0	25.8
30.0	6.0	64.0	2.057	1.127	1.327	49.1	67.2	25.8
5.0	35.0	60.0	2.651	1.163	1.224	38.3	18.2	28.4

Table XXI

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

CALCULATED BY MARGULES THREE-SUFFIX EQUATIONS

150° C C = 0.958

Liquid Composition Mol %							Vapor Comp. Mol %	
A	M	W	γ'_A	γ'_M	γ'_W	π	A	W
47.5	47.5	5.0	1.206	1.073	1.644	208.5	48.3	2.8
45.0	45.0	10.0	1.219	1.056	1.700	202.9	47.3	6.0
42.5	42.5	15.0	1.234	1.038	1.731	197.5	46.1	9.5
40.0	40.0	20.0	1.254	1.019	1.739	192.6	45.1	13.0
37.5	37.5	25.0	1.281	1.003	1.754	189.1	43.8	16.7
35.0	35.0	30.0	1.316	0.990	1.692	183.7	43.0	19.8
32.5	32.5	35.0	1.364	0.982	1.645	179.7	42.1	23.0
30.0	30.0	40.0	1.428	0.980	1.587	176.0	41.4	25.8

Table XXII

VAPOR-LIQUID EQUILIBRIUM OF ACETONE-METHANOL-WATER

CALCULATED BY MARGULES THREE SUFFIX EQUATIONS

200° C C = 1.136

Liquid Comp., Mol %							Vapor Comp., Mol %	
A	M	W	γ'_A	γ'_M	γ'_W	π	A	W
47.5	47.5	5.0	1.195	1.081	1.383	607	47.8	2.9
45.0	45.0	10.0	1.195	1.070	1.475	580	46.0	6.4
42.5	42.5	15.0	1.196	1.056	1.543	558	44.1	10.3
40.0	40.0	20.0	1.200	1.040	1.587	539	42.2	14.6
37.5	37.5	25.0	1.210	1.024	1.606	536	41.7	18.5
35.0	35.0	30.0	1.228	1.011	1.603	521	39.9	22.7

Table XXIII

ACTIVITY COEFFICIENT CORRECTION FACTORS FOR ACETONE

$$\log Z_A = (P_A - \pi)(v_A - B_A)/(2.303\ RT)$$

100°C			150°C			200°C		
Total PSIA	μ	Z	Total PSIA	μ	Z	Total PSIA	μ	Z
15	0.984	1.050	70	0.939	1.110	225	0.838	1.187
20	0.978	1.044	100	0.911	1.077	250	0.813	1.165
25	0.972	1.038	120	0.892	1.054	300	0.752	1.121
30	0.966	1.032	140	0.873	1.032	350	0.701	1.067
35	0.960	1.026	160	0.851	1.010	400	0.650	1.012
40	0.954	1.019	180	0.830	0.988	450	0.596	0.958
50	0.942	1.006	200	0.808	0.965	500	0.548	0.907
60	0.930	0.992						

Table XXIV

ACTIVITY COEFFICIENT CORRECTION FACTORS FOR METHANOL

$$\log Z_M = (P_M - \pi)\ (\ v_M - B_M)/\ (2.303\ RT)$$

100° C			150° C			200° C		
Total PSIA	μ	Z	Total PSIA	μ	Z	Total PSIA	μ	Z
15	0.989	1.030	70	0.966	1.078	225	0.913	1.186
20	0.986	1.025	100	0.950	1.061	250	0.902	1.173
25	0.983	1.020	120	0.938	1.050	300	0.878	1.149
30	0.980	1.016	140	0.927	1.037	350	0.851	1.125
35	0.977	1.012	160	0.915	1.025	400	0.823	1.099
40	0.973	1.008	180	0.903	1.012	450	0.788	1.074
50	0.966	1.000	200	0.891	1.000	500	0.752	1.045
60	0.959	0.993						

Table XXV

ACTIVITY COEFFICIENT CORRECTION FACTORS FOR WATER

$$\log Z_W = (P_W - \pi)(v_W - B_W)/(2.303\ RT)$$

100°C			150°C			200°C		
Total PSIA	μ	Z	Total PSIA	μ	Z	Total PSIA	μ	Z
15	0.995	1.000	70	0.979	1.000	225	0.944	1.002
20	0.992	1.000	100	0.969	0.989	250	0.937	0.993
25	0.990	0.995	120	0.964	0.983	300	0.924	0.979
30	0.988	0.993	140	0.957	0.976	350	0.910	0.964
35	0.986	0.991	160	0.950	0.969	400	0.897	0.950
40	0.985	0.990	180	0.945	0.962	450	0.883	0.934
50	0.981	0.984	200	0.938	0.955	500	0.868	0.921
60	0.976	0.980						

X

APPENDIX

SAMPLE CALCULATIONS

1. Uncorrected activity coefficients from vapor-liquid equilibrium data.

Data of Run 6 of the acetone-water system at 100°C.

$$\gamma_A = \pi y_A / P_A x_A$$

where

γ_A = uncorrected activity coefficient for acetone

π = total pressure, psia

P_A = vapor pressure of acetone at 100°C.

y_A = mol fraction of acetone in vapor

x_A = mol fraction of acetone in liquid.

$$\gamma_A = (35.5)(0.613)/(53.9)(0.082)$$
$$= \underline{\underline{4.924}}$$

2. The correction factor Z.

(1). The second virial coefficient from compressibility factors.

Acetone at 100°C and total pressure of 35.0 psia

$P_r = 35.0/690.4 = 0.0434$

$T_r = 373.2/508.2 = 0.732$

Compressibility factor = 0.960

Ideal molar volume $V_i = RT/P$

$= (1206.3)(373.2)/(35.0)$

$= 12,856$ cc/mol

The second virial coefficient B

$B = V_i(C-1)$

$= 12,856\ (0.960 - 1)$

$= -514.24$

(2). The liquid specific volume $\underline{v}$

$$v = \text{mol. wt./density} \qquad \text{at } 100^{\circ}C$$

$$= 58.08/0.693$$

$$= \underline{\underline{83.78}} \text{ cc/mol}$$

(3). The correction factor $\underline{Z}$

$$\log \underline{Z} = (P-\pi)(v-B)/(2.303\ RT)$$

$$= \frac{(53.9 - 35.0)(83.78 + 5.4.24)}{(2.303)(1206.3)(373.2)}$$

$$= 0.01094$$

$$\underline{Z} = \underline{\underline{1.026}}$$

3. Thermodynamic activity coefficient

$$\gamma'_A = \pi y_A Z_A / P_A x_A$$

$$\gamma'_A = \gamma_A Z_A$$

$$\gamma'_A = (4.924)(1.024) = \underline{\underline{5.042}}$$

4. Partial molal heat of solution $\underline{\underline{L}}$

For acetone-water system at 40 mol per cent acetone in liquid.

Temperature range from 100°C to 150°C

Plot $\log \gamma'$ vs. $1/T$ and assume straight line between points at 100° and 150°, calculate slope.

$$\text{Slope} = \frac{\log \gamma'_{100^{\circ}} - \log \gamma'_{150^{\circ}}}{(1/373.2) - (1/423.2)}$$

$$= \frac{\log 1.651 - \log 1.470}{(1/373.2) - (1/423.2)}$$

$$= \underline{\underline{156.9}}$$

Partial heat of solution

$$\bar{L} = (2.303)(1.987)(\ d \log \gamma' / d(1/T)$$

$$= (2.303)(1.987)(156.9)$$

$$= \underline{\underline{718 \text{ calories}}} \text{ per mol acetone dissolved.}$$

5. The integral heat of solution.

The integral heat of solution was calculated from the mean partial heat of solution at a specified concentration. This was determined by determining the mean ordinate under the curve relating the partial heat of solution, as ordinates, to the concentration expressed as mols solute per mol of solvent.

For 40 mol per cent acetone in liquid

$L_{int.}$ = (mol fraction solute)(mean partial heat of solution)

= (0.40)(910)

= 364 calories per mol of solution containing 40 mol per cent acetone.

6. The mol fraction of a specified component in the vapor in equilibrium with a liquid of known composition, calculated from activity coefficients.

Acetone-methanol binary at 150°, 25 mol per cent acetone in the liquid phase.

$$\gamma'_A = 1.210 \qquad \gamma'_M = 1.058$$

First approximation, assume Z_A and $Z_M = 1$

Calculate the total pressure

$$\pi = \gamma'_A P_A x_A / Z_A + \gamma'_M P_M x_M / Z_M$$

$$= (1.210)(168.9)(0.25) + (1.058)(199.3)(0.75)$$

$$= \underline{\underline{207.7 \text{ psia}}}$$

At 208 psia obtain the correction factors Z,

$$Z_A = 0.955 \qquad Z_M = 0.993$$

Recalculate the total pressure using these Z's

$$\pi = \frac{(1.210)(168.9)(0.25)}{(0.995)} + \frac{(1.058)(199.3)(0.75)}{(0.993)}$$

$$\pi = \underline{\underline{212.8 \text{ psia}}}$$

Calculate the mol fraction acetone in the vapor

$$y_A = \frac{\gamma'_A P_A x_A / Z_A}{\gamma'_A P_A x_A / Z_A + \gamma'_M P_M x_M / Z_M}$$

$$= \frac{(1.210)(168.9)(0.25)/(0.955)}{\frac{(1.210)(168.9)(0.25)}{(0.955)} + \frac{(1.058)(199.3)(0.75)}{(0.993)}}$$

$$= \underline{\underline{0.251}}$$

7. Calculation of the ternary constant C by the Margules 3-suffix ternary equations.

The ternary constant C is obtained by solving the Margules equation using known binary end constants and one experimental ternary point.

$$\log \gamma_1 = x_2^2 \left[A_{1-2} + 2x_1(A_{2-1} - A_{1-2})\right] + x_3^2 \left[A_{1-3} + 2x_1 (A_{3-1} - A_{1-3})\right]$$
$$+ x_2 x_3 \left[A_{2-1} + A_{1-3} - A_{3-2} + 2x_1 (A_{3-1} - A_{1-3}) + 2x_3 (A_{3-2} - A_{2-3} - C (1-2x_1)\right]$$

$$\log 1.820 = (0.440)^2 \left[0.1446 + (2)(0.144)(0.3075 - 0.1446)\right]$$
$$+ (0.416)^2 \left[0.9661 + (2)(0.144)(0.5776 - 0.9661)\right]$$
$$+ (0.440)(0.416) \left[0.3075 + 0.9661 - 0.1553 + (2)(0.144)(0.5776 - 0.9661) + (2)(0.416)(0.1553 - 0.4417 - C (1-0.288)\right]$$

Solve for C

$$C = \underline{\underline{0.502}}$$

8. To calculate thermodynamic ternary activity coefficients by the Margules 3-suffix equations with known ternary constant C and specified liquid composition.
Proceed as above, and solve equation for log γ

NOMENCLATURE

$\underline{a}$	=	Activity
A_{1-2} A_{2-1}	=	Binary end constants for the Margules 3-suffix ternary equations for components 1 and 2
A, B	=	End constants in the van Laar and Margules binary equations
B_1	=	Second virial coefficient in the equation of state for component 1
$\underline{C}$	=	Ternary constant in Margules 3-suffix equation
f	=	Fugacity
f^o	=	Fugacity of pure liquid
G	=	Molar free energy
$\overline{G}$	=	Partial molar free energy
G^o	=	Molar free energy of pure component
G_T	=	Total free energy of specified system
ΔG	=	Non ideality excess free energy term
$\overline{L}$		Partial molal heat of solution, calories per mol of solute
L_i	=	Integral heat of solution, calories per mol solution
N	=	Number of mols of a component
P	=	Vapor pressure of pure component, psia
π	=	Total pressure, psia
R	=	Gas constant
T	=	Temperature, ^oK
v	=	Liquid specific volume, cc/mol
V_i	=	Ideal gas volume, V = RT/P
x	=	Mol fraction of component in liquid phase

y = Mol fraction of component in vapor phase

Z = Correction factor for vapor non-ideality and pressure effects on liquid phase

γ = Uncorrected activity coefficient

γ' = Thermodynamic activity coefficient

μ = Compressibility factor

Subscripts

1, A = Acetone

2, M = Methanol

3, W = Water

XI

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